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Formation and Structure of Cyclic Five-Coordinated Antimony Derivatives. The First Square-Pyramidal Geometry for a Bicyclic Stiborane[1,2]

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Stiboranes $Ph_3Sb(O_2C_6Cl_4)$ (**1**) and $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot 0.25C_6H_6\cdot 0.25CH_2Cl_2$ (**2**) were formed by the oxidative-addition reaction of tetrachloro-*o*-benzoquinone with the corresponding stibole. Reaction of Ph_3SbCl_2 with naphthalenediol in the presence of Et_3N led to the isolation of the six-coordinated hypervalent anionic stiborane $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**3**). The stiboranes **2** and **3** are new compounds with **2** being the first unsaturated bicyclic five-coordinated antimony derivative structurally studied. X-ray analysis revealed a trigonal-bipyramidal structure for **1**, a rectangular-pyramidal geometry for **2**, and a distorted-octahedral form for **3**. The geometries found for **1** and **2** are considered relatively devoid of lattice effects compared to that for the related monohydrate composition $[Ph_3Sb(O_2C_6H_4)]_2\cdot H_2O$. The naphthalene derivative **3** contains a long Sb–Cl bond, which provides this derivative with its octahedral character. In the context of these and other examples, it is concluded that five-coordinated antimony exhibits a high degree of molecular nonrigidity and that the normally less stable rectangular pyramid forms, as with other group 4 (14) and 5 (15) elements, whenever two unsaturated five-membered rings are present with like atoms in any one ring directly bonded to the central atom. Stiborane **1** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.345 (2) Å, b = 10.904 (3) Å, c = 21.178 (3) Å, β = 102.24 (1)°, and Z = 4. **2** crystallizes in the triclinic space group $P\bar{1}$ with a = 13.566 (4) Å, b = 13.762 (4) Å, c = 14.086 (3) Å, α = 90.10 (2)°, β = 105.85 (2)°, γ = 107.20 (2)°, and Z = 4. **3** crystallizes in the monoclinic space group $C2/c$ with a = 28.600 (5) Å, b = 12.685 (2) Å, c = 18.515 (4) Å, β = 113.58 (1)°, and Z = 8. The final conventional unweighted agreement factors were 0.039 (**1**), 0.035 (**2**), and 0.039 (**3**).

Introduction

The square-pyramidal structure associated with $SbPh_5$[3] is unique among five-coordinated group 4 (14[41]) and 5 (15[41]) molecules containing solely monodentate ligands.[4] This geometry has normally been found for other elements of these families when two unsaturated five-membered ring systems are present containing like atoms in any one ring directly bound to the central atom.[5,6] Later Brabant et al. reported the crystal structures of the cyclohexane solvate of antimony pentaphenyl, $SbPh_5\cdot 0.5C_6H_{12}$,[7] and the related tolyl derivative $(CH_3C_6H_4)_5Sb$[8] as trigonal bipyramidal. These results suggested that the square-pyramidal structure for $SbPh_5$ was lattice-stabilized. Calculations[9] lent support to this assertion.

When cyclic derivatives are considered, an additional example of a square-pyramidal geometry is revealed in the partially hydrated substance $[Ph_3Sb(O_2C_6H_4)]_2\cdot H_2O$,[10] which contains both five- and six-coordinated antimony atoms in the crystal. Again the presence of this structural form is unusual in that only one ring system is present. For each of the elements P,[11] As,[12] Si,[13] Ge,[14] and Sn,[15,16] derivatives possessing a square-pyramidal geometry have two such ring systems.[4,6] The possibility arises that hydrogen bonding present in the hydrated derivative may act to stabilize the square pyramid for the five-coordinated antimony atom contained therein.

Compared to phosphorus[4,11] and arsenic[4,12,17] in the five-coordinated state, antimony[3,7-10,18] has not received a great deal of attention. It remains to establish the applicability of structural principles found for five-coordinated derivatives of other main-group elements and to ascertain the importance of lattice effects as a structural determinant. Toward this end, we report new pentacoordinated derivatives of antimony containing one and two cyclic components, $Ph_3Sb(O_2C_6Cl_4)$ (**1**) and $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot 0.25C_6H_6\cdot 0.25CH_2Cl_2$ (**2**), respectively. The former compound **1** resembles the hydrated derivative[10] in composition but lacks hydrogen bonding as a structural influence. The latter compound **2** provides the first example of a stiborane containing two five-membered rings with unsaturation. The crystal structures of **1** and **2** are reported as well as that for a third derivative, $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**3**), exhibiting hydrogen bonding.

Experimental Section

Triphenylantimony dichloride (Alfa), 2,3-naphthalenediol, tetrachloro-*o*-benzoquinone, *o*-dibromobenzene, 4-nitrocatechol, and *n*-butyllithium (Aldrich) were used as received. Antimony trichloride and triphenyl antimony (Aldrich) were purified by sublimation prior to use. Phenylantimony dichloride was prepared according to a previous procedure.[19] The solvents were purified by standard procedures.[20]

Proton NMR spectra were recorded on a Varian 300-MHz instrument operating in the FT-pulse mode. Chemical shifts were measured in ppm relative to tetramethylsilane as the internal standard.

Preparation of Triphenyl(tetrachlorocatecholato)antimony(V), $Ph_3Sb(O_2C_6Cl_4)$ (1). Triphenylantimony (1.03 g, 2.92 mmol) was dissolved in dry benzene (30 mL). (*Caution*! Benzene is a class A carcinogen and should be used in a hood equipped with a good exhaust system.) Tetrachloro-*o*-benzoquinone (0.72 g, 2.93 mmol) dissolved in 50 mL of dry benzene was added dropwise to the antimony solution over a period of 40 min under an atmosphere of dry argon. The dark red color

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of the quinone lightened as each drop came into contact and reacted with the triphenylantimony solution. After the addition was complete, the reaction mixture became yellowish brown. Stirring was continued for 12 h. Removal of solvent under vacuum yielded a solid material: yield 1.5 g, 85.7%. It was recrystallized from chloroform and Skelly B (a mixture of aliphatic hydrocarbons, 88–98 °C fraction, Home Oil Co., Wichita, KS) (1:2) at 0 °C to yield yellow crystals suitable for X-ray analysis; mp 183–185 °C (lit.[21] mp 185 °C). Anal. Calcd for $C_{24}H_{15}O_2Cl_4Sb$: C, 48.13; H, 2.52; Cl, 23.67. Found: C, 47.96; H, 2.35; Cl, 23.73. ^1H NMR ($CDCl_3$): 7.80 (m, 2 H); 7.60 (m, 3 H).

Preparation of Phenyl(2,2′-biphenylene)(tetrachlorocatecholato)antimony(V)–0.25-Benzene–0.25-Methylene Chloride, $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot0.25C_6H_6\cdot0.25CH_2Cl_2$ (2). (a) Preparation of Phenyl(2,2′-biphenylene)stibine, $(Ph)(C_{12}H_8)Sb^{III}$. 2,2′-Dibromobiphenyl[22] (4.0 g, 12.8 mmol) was dissolved in 100 mL of anhydrous ether under an atmosphere of argon at 0 °C. To this was added 12.0 mL of a 2.5 m solution of *n*-butyllithium (30.0 mmol), dissolved in 50 mL of anhydrous ether, over a period of 30 min. The reaction mixture was allowed to come to room temperature and was stirred for 12 h. To the 2,2′-dilithiobiphenyl thus formed[22] was added phenylantimony dichloride (3.5 g, 13.0 mmol) dissolved in 160 mL of benzene over a period of 1 h. (*Caution*! Benzene is a class A carcinogen and should be used in a hood equipped with a good exhaust system.) The reaction mixture became milky white. It was heated under reflux for 3 h. The reaction was stopped and the mixture was allowed to come to room temperature and treated with a saturated solution of ammonium chloride in water (100 mL). The organic layer was separated and stored over anhydrous sodium sulfate. The aqueous layer was extracted with 4 × 50 mL of benzene, and the extracts were combined with the organic layer. After this solution was dried for 3 h, the solvent was removed to yield an oil. It was pumped under vacuum and dissolved in a mixture of ethanol (5 mL) and ether (10 mL), and the solution was kept in an ice bath. After about 5 h a pale yellow solid was isolated. From the mother liquor second and third crops could be isolated: total yield of the stibine 2.9 g, 64.4%; mp 98–101 °C (lit.[23] mp 98–101 °C).

(b) Reaction of Phenyl(2,2′-biphenylene)stibine with Tetrachloro-*o*-benzoquinone. Phenyl(2,2′-biphenylene)stibine (0.36 g, 1.03 mmol) was dissolved in 150 mL of diethyl ether under an atmosphere of dry argon. This solution was cooled to 0 °C, and tetrachloro-*o*-benzoquinone dissolved in the same solvent (100 mL) was added very slowly, dropwise, over a period of 1 h. The intense red color of the quinone started disappearing as soon as it came into contact with the antimony solution, indicating that the oxidative addition was taking place. Eventually, after all the quinone was added, the reaction mixture assumed a yellowish color. It was stirred at room temperature for 12 h and heated under reflux for 12 h more to ensure the completion of reaction. Removal of solvent from the pale yellow-green solution yielded a viscous oil. Trituration with Skelly B afforded a solid: 0.55 g; mp 220 °C dec. It was recrystallized from a mixture of methylene chloride and Skelly B (1:2) at 25 °C to give yellow crystals of the compound **2**: yield 0.35 g, 57%; mp 250–251 °C. Anal. Calcd for $C_{24}H_{13}O_2Cl_4Sb$: C, 48.29; H, 2.20. Found: C, 48.51; H, 2.47. ^1H NMR ($CDCl_3$): 8.06 (m), 7.54 (m).

Preparation of Triethylammonium Triphenyl(2,3-naphthalenediolato)chloroantimonate(V), $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (3). To a mixture of triphenylantimony dichloride (1.53 g, 3.74 mmol) and 2,3-naphthalenediol (0.60 g, 3.75 mmol) in toluene (200 mL) was added triethylamine (0.76 g, 7.51 mmol). The resulting mixture was stirred for 72 h at room temperature. Filtration yielded a precipitate and a filtrate. Removal of solvent from filtrate yielded a negligible amount of material. The precipitate was worked up as follows.

Water (50 mL) was added to the precipitate, and the mixture was stirred for 10 min to dissolve triethylammonium hydrochloride. The insoluble material was dissolved in acetonitrile (100 mL) and dried (Na_2SO_4). Removal of solvent yielded a pale yellow solid. It was redissolved in a minimum amount of hot acetonitrile (4 mL) and crystallized at room temperature to afford compound **3**: 1.1 g, 45.5%; mp 182–184 °C. Anal. Calcd for $C_{34}H_{37}NO_2ClSb$: C, 62.94; H, 5.75; N, 2.16. Found: C, 63.05; H, 5.48; N, 2.09. ^1H NMR ($CDCl_3$): 7.0–8.0 (m, 21 H), 3.0 (q, 6 H), 1.2 (t, 9 H).

Crystallography. All X-ray crystallographic studies were done with an Enraf-Nonius CAD4 diffractometer and graphite-monochromated molybdenum radiation ($\lambda_{K\alpha_1}$ = 0.709 30 Å, $\lambda_{K\alpha_2}$ = 0.713 59 Å) at an ambient temperature of 23 ± 2 °C. Details of the experimental and computational procedures have been described previously.[24] Crystals were mounted inside thin-walled glass capillaries, which were sealed as a precaution against moisture sensitivity.

X-ray Crystallographic Studies for 1. The crystal used for the X-ray study was cut from a larger, chunky, polyfaceted yellow crystal and had dimensions of 0.28 × 0.30 × 0.38 mm.

Crystal Data: $Ph_3SbO_2C_6Cl_4$, monoclinic, space group $P2_1/n$ (alternate setting of $P2_1/c$ (C_{2h}^5, No. 14)[25]), a = 10.345 (2) Å, b = 10.904 (3) Å, c = 21.178 (3) Å, β = 102.24 (1)°, Z = 4, and $\mu_{\text{Mo K}\alpha}$ = 1.669 mm^{-1}. A total of 4092 independent reflections ($+h,+k,\pm l$) was measured with the θ–2θ scan mode for $2° \le 2\theta_{\text{Mo K}\alpha} \le 50°$. No corrections were made for absorption.

The structure was solved by using conventional Patterson and difference Fourier techniques and was refined by using full-matrix least squares.[26] The 31 independent non-hydrogen atoms were refined anisotropically. The 15 independent hydrogen atoms were included in the refinement as fixed isotropic scatterers with calculated coordinates that were updated as refinement converged so that the final C–H bond lengths were 0.98 Å. The final agreement factors[27] (280 variables) were R = 0.039 and R_w = 0.052 for the 3450 reflections having $I \ge 2\sigma_I$.

X-ray Crystallographic Studies for 2. Conditions for data collection and refinement were the same as described for **1**, unless otherwise noted. The crystal used for data collection was cut from a yellow lath and had dimensions of 0.15 × 0.30 × 0.35 mm.

Crystal Data: $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot0.25C_6H_6\cdot0.25CH_2Cl_2$, triclinic, space group $P\bar{1}$ (C_i^1, No. 2),[28] a = 13.566 (4) Å, b = 13.762 (4) Å, c = 14.086 (3) Å, α = 90.10 (2)°, β = 105.85 (2)°, γ = 107.20 (2)°, Z = 4, and $\mu_{\text{Mo K}\alpha}$ = 1.679 mm^{-1}. A total of 5500 independent reflections ($+h,\pm k,\pm l$) was measured for $2° \le 2\theta_{\text{Mo K}\alpha} \le 43°$.

The unit cell contains one molecule of benzene with crystallographic C_i symmetry and one molecule of CH_2Cl_2, which is disordered about an inversion center in such a way that the Cl atoms are inversion-related. There are two independent stiborane molecules in the asymmetric unit. The asymmetric unit thus contains 66 non-hydrogen atoms in full occupancy and one carbon atom in half-occupancy. These 67 independent atoms were refined anisotropically. The 26 hydrogen atoms of the two independent stiboranes were treated as described for **1**. Hydrogen atoms of the molecules of solvation were omitted from the refinement. The final agreement factors[27] (604 variables) were R = 0.035 and R_w = 0.043 for the 4321 reflections having $I \ge 2\sigma_I$.

X-ray Crystallographic Studies for 3. Conditions for data collection and refinement were the same as described for **1**, unless otherwise noted. Crystals of **3**, colorless flattened-hexagonal prisms that appear pale yellow in bulk, proved to be twinned. A single crystal with approximate dimensions of 0.13 × 0.23 × 0.35 mm, obtained by cleaving and cutting a twin, was used for the X-ray study.

Crystal Data: $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15),[29] a = 28.600 (5) Å, b = 12.685 (2) Å, c = 18.515 (4) Å, β = 113.58 (1)°, Z = 8, and $\mu_{\text{Mo K}\alpha}$ = 1.025 mm^{-1}. A total of 3514 independent reflections ($+h,+k,\pm l$) was measured for $2° \le 2\theta_{\text{Mo K}\alpha} \le 43°$.

The 39 independent non-hydrogen atoms were refined anisotropically. The 28 independent hydrogen atoms with calculable coordinates were treated as described for **1**, except that the amino hydrogen atom was refined as an isotropic scatterer. Methyl-group hydrogen atoms were omitted from the refinement. The final agreement factors[27] (356 variables) were R = 0.039 and R_w = 0.053 for the 2560 reflections having $I \ge 2\sigma_I$.

Results

The atom labeling schemes for **1–3** are given in the ORTEP plots of Figures 1–3, respectively. Atomic coordinates are given in Tables I–III, while selected bond lengths and angles are given in Tables IV–VI. Thermal parameters, hydrogen atom parameters, additional bond lengths and angles, and deviations from selected least-squares mean planes are provided as supplementary material.

Discussion

Synthesis. Stiboranes **2** and **3** are new compounds. In fact, **2** represents the first synthesis of a pentacoordinated antimony

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(26) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{1/2} = 2F_oLp/\sigma_I$. Mean atomic scattering factors were taken from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV pp 72–98. Real and imaginary dispersion corrections for Sb, Cl, and O were taken from the same source, pp 149–150.

(27) $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$.

(28) Reference 25, p 75.

(29) Reference 25, p 101.

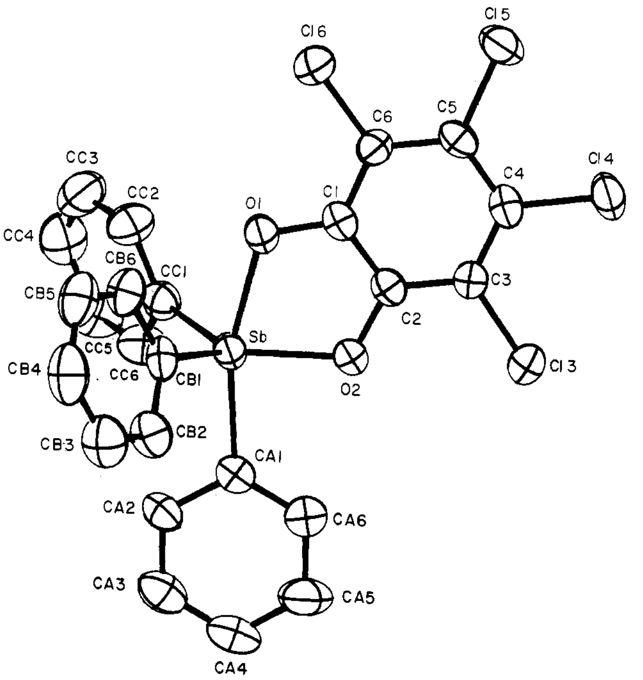


Figure 1. ORTEP plot of $Ph_3Sb(O_2C_6Cl_4)$ (**1**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

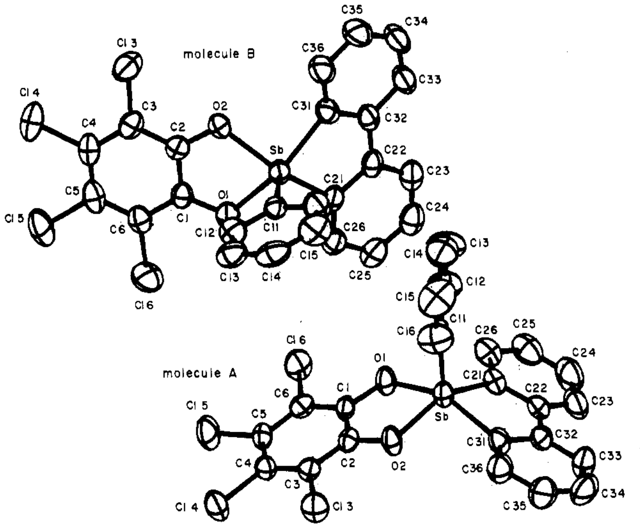


Figure 2. ORTEP plot showing the two independent $(Cl_4C_6O_2)(C_{12}H_8)$-SbPh molecules for **2** with thermal ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for purposes of clarity.

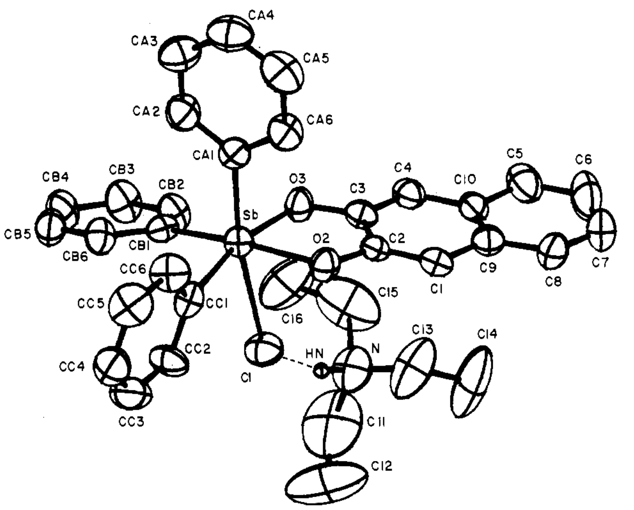


Figure 3. ORTEP plot of $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**3**) with thermal ellipsoids at the 50% probability level. Hydrogen atoms, except for HN, which is represented by a sphere of arbitrary radius, have been omitted for purposes of clarity. The hydrogen-bonding interaction is shown as a dashed line.

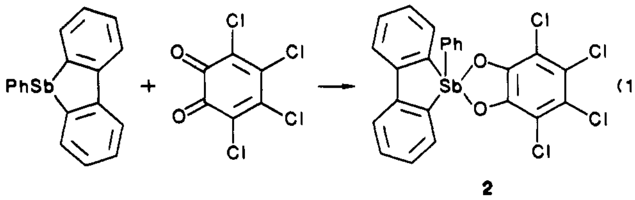
Table I. Atomic Coordinates in Crystalline $Ph_3Sb(O_2C_6Cl_4)$ (**1**)[a]

atom	coordinates		
type[b]	10^4x	10^4y	10^4z
Sb	3123.1 (3)	751.7 (3)	1495.0 (2)
Cl3	5883 (1)	68 (2)	3685 (1)
Cl4	8687 (1)	−1055 (2)	3657 (1)
Cl5	9390 (1)	−1655 (1)	2335 (1)
Cl6	7427 (2)	−885 (2)	1045 (1)
O1	4940 (3)	227 (4)	1278 (2)
O2	4276 (3)	540 (3)	2385 (2)
C1	5838 (4)	−81 (4)	1799 (2)
C2	5498 (4)	99 (4)	2398 (2)
C3	6366 (5)	−186 (5)	2966 (2)
C4	7586 (5)	−692 (4)	2951 (2)
C5	7926 (5)	−931 (4)	2360 (2)
C6	7043 (5)	−606 (4)	1780 (2)
CA1	1604 (5)	1214 (5)	2003 (2)
CA2	343 (5)	1423 (5)	1628 (3)
CA3	−685 (5)	1723 (5)	1931 (3)
CA4	−463 (6)	1813 (5)	2597 (3)
CA5	805 (6)	1635 (7)	2961 (3)
CA6	1827 (6)	1319 (6)	2663 (3)
CB1	3180 (5)	2369 (5)	945 (2)
CB2	2535 (6)	3424 (5)	1109 (3)
CB3	2512 (7)	4472 (6)	742 (3)
CB4	3111 (7)	4476 (6)	216 (3)
CB5	3742 (6)	3432 (6)	51 (3)
CB6	3773 (6)	2370 (5)	425 (2)
CC1	2256 (5)	−728 (4)	904 (2)
CC2	2818 (6)	−1140 (6)	402 (3)
CC3	2201 (7)	−2046 (6)	−2 (3)
CC4	1033 (7)	−2550 (5)	80 (3)
CC5	475 (6)	−2158 (6)	575 (3)
CC6	1077 (6)	−1252 (5)	983 (3)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 1.

derivative containing a mixed-ligand spirocyclic system and also represents the first structural determination of a five-coordinated spirocyclic antimony compound having aromatic substituents.

The spirobicyclic stiborane **2** is synthesized by an oxidative-addition reaction of tetrachloro-*o*-benzoquinone with phenyl(2,2′-biphenylene)stibine analogous to the preparation of **1** (eq 1). Such oxidative-addition reactions are fairly commonplace in phosphorus chemistry and have been used with great success in the synthesis of a number of unsymmetrical cyclic compounds.[30,31] While tricoordinated phosphorus can easily be oxidized by weak oxidative-addition agents such as benzil, a similar reaction with phenyl(2,2′-biphenylene)stibine only yields the starting materials.[32] It seems that the presence of electronegative groups on the diketone is necessary for the reaction to proceed.



(1)

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The reaction of triphenylantimony dichloride with naphthalenediol using 2 equiv of the tertiary amine afforded the six-co-

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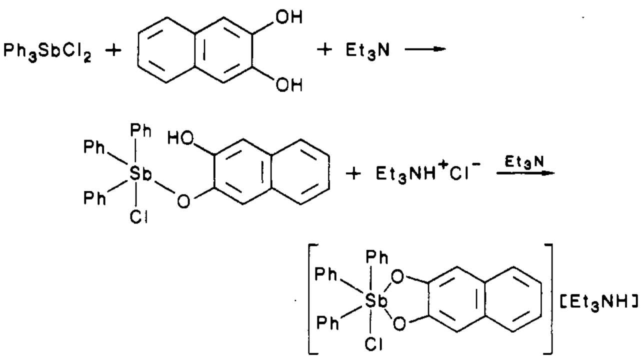
Table II. Atomic Coordinates in Crystalline $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot 0.25C_6H_6\cdot 0.25CH_2Cl_2$ (**2**)[a]

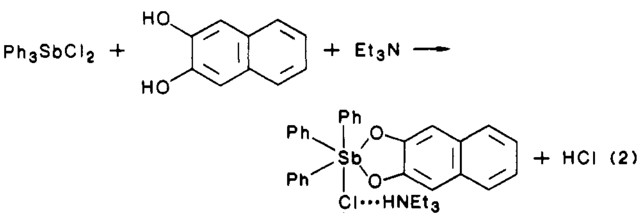
atom	coordinates		
type[b]	10^4x	10^4y	10^4z
SbA	2259.2 (3)	514.7 (3)	7791.2 (3)
SbB	5254.1 (3)	2890.2 (3)	4197.2 (3)
ClA3	4332 (1)	−1947 (1)	8676 (1)
ClA4	6834 (1)	−848 (1)	9504 (1)
ClA5	7715 (1)	1533 (1)	9566 (1)
ClA6	6111 (1)	2792 (1)	8857 (1)
ClB3	8116 (1)	3982 (1)	2474 (1)
ClB4	10374 (1)	3968 (2)	3828 (2)
ClB5	10627 (1)	3449 (2)	6029 (2)
ClB6	8615 (2)	2956 (2)	6854 (1)
OA1	3812 (3)	1485 (3)	8223 (3)
OA2	3084 (3)	−507 (3)	8151 (3)
OB1	6624 (3)	3001 (3)	5342 (3)
OB2	6416 (3)	3444 (3)	3510 (3)
CA1	4548 (4)	990 (4)	8513 (4)
CA2	4160 (4)	−76 (4)	8475 (4)
CA3	4859 (4)	−633 (4)	8764 (4)
CA4	5962 (5)	−142 (4)	9115 (4)
CA5	6345 (4)	904 (4)	9152 (4)
CA6	5644 (5)	1473 (4)	8846 (4)
CA11	1911 (4)	466 (5)	6246 (4)
CA12	1939 (6)	1346 (5)	5769 (5)
CA13	1623 (7)	1323 (6)	4758 (6)
CA14	1293 (6)	421 (7)	4208 (5)
CA15	1252 (7)	−472 (6)	4660 (6)
CA16	1566 (7)	−449 (5)	5671 (6)
CA21	1714 (5)	1636 (5)	8336 (4)
CA22	772 (5)	1161 (5)	8593 (4)
CA23	314 (6)	1784 (6)	8979 (5)
CA24	787 (7)	2839 (6)	9097 (6)
CA25	1682 (6)	3278 (5)	8824 (5)
CA26	2190 (5)	2692 (5)	8442 (5)
CA31	928 (5)	−523 (5)	8123 (4)
CA32	338 (5)	18 (5)	8461 (4)
CA33	−617 (5)	−526 (6)	8640 (5)
CA34	−981 (6)	−1584 (6)	8476 (6)
CA35	−392 (6)	−2107 (6)	8159 (6)
CA36	564 (5)	−1577 (5)	7974 (5)
CB1	7511 (5)	3217 (4)	5037 (4)
CB2	7399 (5)	3445 (4)	4047 (4)
CB3	8286 (5)	3690 (4)	3687 (4)
CB4	9287 (5)	3688 (5)	4292 (5)
CB5	9384 (5)	3455 (4)	5265 (5)
CB6	8507 (5)	3219 (4)	5636 (5)
CB11	4769 (5)	1308 (4)	3838 (4)
CB12	5501 (5)	771 (5)	4015 (5)
CB13	5151 (6)	−278 (5)	3765 (5)
CB14	4074 (7)	−778 (5)	3356 (5)
CB15	3341 (6)	−248 (5)	3167 (6)
CB16	3681 (5)	801 (5)	3412 (5)
CB21	4609 (4)	3402 (4)	5235 (5)
CB22	3847 (4)	3884 (4)	4750 (5)
CB23	3339 (5)	4263 (5)	5334 (5)
CB24	3572 (5)	4173 (5)	6333 (5)
CB25	4325 (5)	3708 (5)	6807 (5)
CB26	4852 (5)	3328 (5)	6242 (5)
CB31	4202 (5)	3515 (4)	3182 (4)
CB32	3643 (4)	3943 (4)	3663 (5)
CB33	2928 (5)	4430 (5)	3105 (5)
CB34	2794 (5)	4434 (6)	2101 (6)
CB35	3325 (6)	3997 (6)	1621 (5)
CB36	4045 (5)	3528 (5)	2170 (5)
CS1	−793 (6)	4290 (5)	327 (6)
CS2	103 (6)	4954 (6)	1015 (6)
CS3	902 (5)	5683 (5)	654 (6)
ClM	−4176 (3)	4636 (3)	689 (3)
CM	−5006 (12)	4333 (8)	−136 (10)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Scheme I

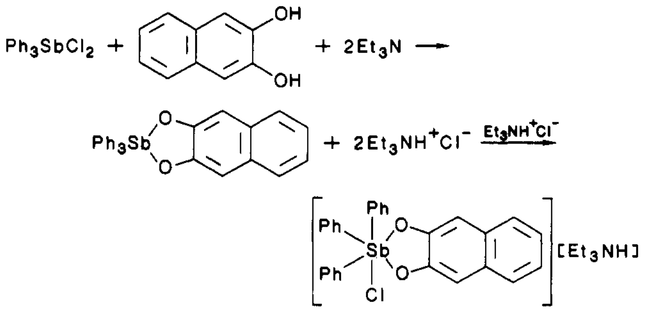


ordinated hypervalent anionic stiborane **3**, instead of a five-coordinated compound (eq 2). Two possible pathways are suggested for the formation of this product. In Scheme I, a condensation reaction is followed by proton abstraction by Et_3N and subsequent cyclization. In Scheme II formation of the five-coordinated antimony compound is envisioned, which then undergoes halide addition. The possibility represented by Scheme II appears less likely since triethylamine hydrochloride, formed in the reaction, would be insoluble in the solvent used (benzene) and would not ionize in it to give the chloride nucleophile.

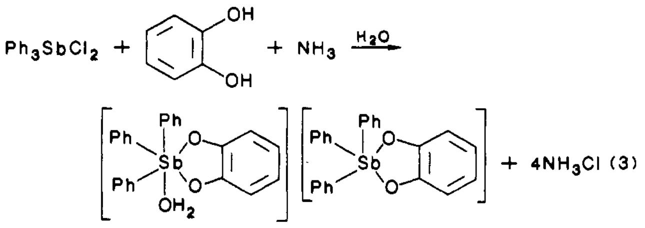


3

Scheme II



The formation of the weak chloride ion association in **3** underscores the ability of antimony(V) compounds to act as Lewis acids and increase their coordination geometry under favorable conditions. In the related reaction between triphenylantimony dichloride and catechol, the product isolated is a cocrystal of triphenylantimony catecholate and its hydrate,[10] resulting in one five- and one six-coordinated antimony atom (eq 3).



Structural Details. The molecular geometry about the antimony atom in the monocyclic stiborane **1** can be referred to a trigonal bipyramid (TBP) having O2, CB1, and CC1 in equatorial positions and O1 and CA1 in axial positions. Distortions away from the idealized trigonal-bipyramidal geometry are modest. The axial

Table III. Atomic Coordinates in Crystalline $[Ph_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**3**)[a]

atom	coordinates		
type[b]	10^4x	10^4y	10^4z
Sb	1466.7 (2)	517.1 (4)	1024.7 (3)
Cl	2005.7 (8)	1404 (2)	2459 (1)
O2	1993 (2)	1350 (4)	760 (3)
O3	2071 (3)	−509 (4)	1421 (3)
C1	2860 (3)	1318 (6)	910 (4)
C2	2450 (3)	872 (5)	992 (4)
C3	2491 (3)	−155 (5)	1343 (4)
C4	2934 (3)	−718 (6)	1578 (4)
C5	3825 (3)	−870 (8)	1695 (5)
C6	4232 (3)	−436 (9)	1595 (6)
C7	4210 (3)	579 (8)	1275 (6)
C8	3767 (3)	1134 (7)	1050 (5)
C9	3333 (3)	736 (6)	1144 (4)
C10	3366 (3)	−269 (6)	1483 (4)
CA1	1158 (3)	−239 (5)	−101 (4)
CA2	759 (3)	−952 (7)	−297 (5)
CA3	559 (3)	−1465 (7)	−1014 (5)
CA4	779 (4)	−1299 (7)	−1549 (5)
CA5	1184 (4)	−628 (8)	−1358 (5)
CA6	1377 (3)	−87 (7)	−648 (4)
CB1	1111 (3)	−421 (5)	1631 (4)
CB2	1373 (3)	−1201 (6)	2143 (4)
CB3	1128 (3)	−1825 (6)	2507 (5)
CB4	631 (3)	−1623 (6)	2375 (5)
CB5	366 (3)	−824 (7)	1868 (5)
CB6	608 (3)	−234 (6)	1507 (4)
CC1	961 (3)	1871 (6)	751 (4)
CC2	939 (3)	2540 (6)	1326 (4)
CC3	568 (3)	3317 (7)	1136 (6)
CC4	218 (3)	3433 (7)	384 (6)
CC5	232 (3)	2757 (7)	−187 (5)
CC6	607 (3)	1995 (6)	−3 (5)
N	3044 (3)	727 (7)	3763 (4)
C11	3096 (5)	1080 (15)	4550 (7)
C12	3020 (6)	2198 (8)	4610 (8)
C13	3368 (4)	1154 (10)	3369 (7)
C14	3938 (4)	1061 (11)	3858 (10)
C15	3061 (6)	−550 (10)	3717 (8)
C16	2641 (5)	−1080 (9)	3753 (8)
HN	2717 (35)	992 (72)	3453 (55)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

Table IV. Selected Bond Lengths (Å) and Angles (deg) in $Ph_3Sb(O_2C_6Cl_4)$ (**1**)[a]

type[b]	length	type	length
Sb–O1	2.107 (3)	Sb–CC1	2.121 (5)
Sb–O2	2.019 (3)	O1–C1	1.327 (5)
Sb–CA1	2.144 (5)	O2–C2	1.347 (5)
Sb–CB1	2.122 (5)		

type	angle	type	angle
O1–Sb–O2	78.2 (1)	Sb–O2–C2	115.2 (3)
O1–Sb–CA1	163.0 (2)	Sb–CA1–CA2	116.7 (4)
O1–Sb–CB1	88.6 (2)	Sb–CA1–CA6	123.2 (4)
O1–Sb–CC1	87.1 (2)	Sb–CB1–CB2	118.2 (4)
O2–Sb–CA1	84.8 (2)	Sb–CB1–CB6	120.8 (4)
O2–Sb–CB1	121.9 (2)	Sb–CC1–CC2	120.3 (4)
O2–Sb–CC1	123.8 (2)	Sb–CC1–CC6	120.9 (4)
CA1–Sb–CB1	100.9 (2)	O1–C1–C6	123.9 (4)
CA1–Sb–CC1	102.2 (2)	O1–C1–C2	116.9 (4)
CB1–Sb–CC1	111.4 (2)	O2–C2–C1	116.5 (4)
Sb–O1–C1	112.8 (3)	O2–C2–C3	122.3 (4)

[a] Numbers in parentheses are estimated standard deviations. [b] atoms are labeled to agree with Figure 1.

bond, Sb–O1, has a length of 2.107 (3) Å, which is, as expected, longer than the corresponding equatorial bond length (Sb–O2 = 2.019 (3) Å). The difference between the axial and equatorial Sb–C bond lengths is not very pronounced. The axial bond, Sb–CA1, has a length of 2.144 (5) Å as compared to the average value of the equatorial Sb–C bond lengths of 2.122 (5) Å. Relative to the equatorial plane defined by the four atoms Sb, O2, CB1, and CC1, the antimony atom is displaced 0.204 Å out of the plane defined by the other three in a direction toward CA1. Relative to the plane of the catechol ligand, the atoms O1, O2, and C1–C6 are coplanar to within ±0.038 Å. However, the antimony atom is displaced 0.228 Å out of this plane in a direction toward CC1.

For the spirobicyclic derivative **2**, there are two independent stiborane molecules. Both have similar molecular geometry about the antimony atom and can best be referred to a rectangular-pyramidal geometry (RP) having the phenyl group in the apical position. Deviations away from the idealized rectangular-pyramidal geometry very nearly follow the pseudorotational coordinate,[33] leading to a trigonal bipyramid having O1 and C31 in axial positions. With use of the dihedral angle method[11,34] to assess displacement, molecule A is displaced an average of 88.0% (88.9% with unit vectors) from the TBP toward the RP. For molecule B, the corresponding displacement is 71.8% (72.6% with unit vectors). In molecule A, the atoms comprising the basal plane of the RP are coplanar to within ±0.046 Å with the antimony atom displaced 0.564 Å out of this plane in a direction toward the apical phenyl group. The trans basal angles have values of 151.0 (2) and 145.9 (2)°. For molecule B, which has more residual trigonal-bipyramidal character, these values are ±0.158 Å, 0.602 Å, 153.1 (2)°, and 139.3 (2)°, respectively. For both molecules, the atoms of the biphenylene ligand are nearly coplanar (±0.053 Å for A and ±0.026 Å for B) with the antimony atom approximately in this plane (0.080 Å for A and 0.023 Å for B).

In the chlorine-containing monocyclic derivative **3**, the antimony atom is hexacoordinated, and the molecular geometry about the antimony atom can be described as distorted octahedral. The Sb–O bond lengths and the Sb–C bond lengths have values very close to the sums of the corresponding covalent radii of 2.07 and 2.18 Å, respectively. The Sb–Cl bond length of 2.724 (2) Å is, however, on the order of 0.3 Å longer than the sum of the covalent radii for Sb and Cl, which is 2.40 Å.[35] Some elongation of the Sb–Cl bond is to be expected since the Cl atom is hydrogen bonded to the ammonium hydrogen atom of the cation. Even when this is taken into consideration, the Sb–Cl bond apparently is the weakest of the bonds to the antimony atom. This is reflected in the geometry about the latter atom, which can be referred to as a rectangular pyramid having CA1 in the apical position, with a sixth weaker interaction due to the chlorine atom causing an increase in the value of the trans basal angles of the RP.

The atoms forming the basal plane of this RP, O2, O3, CB1, and CC1, are coplanar to within ±0.027 Å, with the antimony atom displaced out of this plane by 0.218 Å in a direction toward the apical atom CA1. The trans basal angles O2–Sb–CB1 and O3–Sb–CC1 have values of 162.7 (2) and 166.7 (2)°, respectively, as compared to the idealized value of the trans basal angles for a main-group RP of about 150°.[36,37]

Structural Comparisons. There seems little question that lattice stabilization is responsible for the appearance of a square-pyramidal form for $SbPh_5$. It has been less clear what factors lead to the formation of a square pyramid for the five-coordinated antimony component in the monohydrated composition $[Ph_3Sb(O_2C_6H_4)]_2 \cdot H_2O$ shown in eq 3.

In terms of the dihedral angle method,[34] the geometry around the pentacoordinated antimony atom in the latter compound is displaced 85.3% (using unit vectors) from the TBP toward the RP.[18] The trans basal angles[10] of 147.4 (2) and 154.9 (1)° are approaching the ideal RP value of 150°. Hence, the structure shows a high degree of stabilization near the rectangular-pyramidal geometry normally found[36,37] for a main-group pentacoordinated element.

The structure of the related antimony derivative **1** studied here, containing a tetrachloro-substituted catecholate unit in place of

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Table V. Selected Bond Lengths (Å) and Bond Angles (deg) for $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot0.25C_6H_6\cdot0.25CH_2Cl_2$ (**2**)[a]

type[b]	length: molecule A	length: molecule B	type	length: molecule A	length: molecule B
Sb–O1	2.055 (4)	2.067 (4)	O1–C1	1.344 (6)	1.338 (7)
Sb–O2	2.027 (4)	2.032 (4)	O2–C2	1.346 (6)	1.340 (7)
Sb–C21	2.120 (6)	2.111 (6)	C22–C32	1.499 (9)	1.486 (8)
Sb–C31	2.111 (6)	2.106 (6)			
Sb–C11	2.095 (6)	2.096 (6)			

type	angle: molecule A	angle: molecule B	type	angle: molecule A	angle: molecule B
O1–Sb–C31	151.0 (2)	153.1 (2)	Sb–O1–C1	112.8 (3)	112.5 (3)
O2–Sb–C21	145.9 (2)	139.3 (2)	Sb–O2–C2	113.8 (3)	113.7 (3)
C11–Sb–O1	101.3 (2)	97.8 (2)	O1–C1–C2	117.0 (5)	116.9 (5)
C11–Sb–O2	103.4 (2)	103.6 (2)	O2–C2–C1	116.8 (5)	116.5 (5)
C11–Sb–C31	107.4 (2)	108.7 (2)	Sb–C21–C22	109.7 (4)	109.8 (4)
C11–Sb–C21	110.5 (2)	116.5 (2)	Sb–C31–C32	109.7 (4)	110.6 (4)
O1–Sb–O2	79.7 (1)	79.1 (1)	C21–C22–C32	118.5 (5)	117.9 (5)
C21–Sb–C31	83.9 (2)	83.4 (2)	C31–C32–C22	118.1 (5)	118.3 (5)
O1–Sb–C21	90.3 (2)	88.3 (2)	C23–C22–C32	124.2 (6)	125.1 (6)
O2–Sb–C31	89.3 (2)	90.6 (2)	C33–C32–C22	123.3 (6)	123.1 (6)
			Sb–C21–C26	127.4 (5)	128.8 (4)
			Sb–C31–C36	129.2 (5)	127.7 (5)

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 2.

Table VI. Selected Bond Lengths (Å) and Angles (deg) in $[(C_6H_5)_3Sb(Cl)(O_2C_{10}H_6)][Et_3NH]$ (**3**)[a]

type[b]	length	type	length
Sb–Cl	2.724 (2)	Sb–CC1	2.171 (7)
Sb–O2	2.052 (4)	O2–C2	1.346 (8)
Sb–O3	2.050 (4)	O3–C3	1.345 (8)
Sb–CA1	2.138 (7)	Cl---HN	2.19 (9)
Sb–CB1	2.151 (7)		

type	angle	type	angle
Cl–Sb–O2	80.6 (1)	O3–Sb–CB1	88.2 (2)
Cl–Sb–O3	81.1 (1)	O3–Sb–CC1	166.7 (2)
Cl–Sb–CA1	171.0 (2)	CA1–Sb–CB1	99.4 (3)
Cl–Sb–CB1	85.5 (2)	CA1–Sb–CC1	98.7 (3)
Cl–Sb–CC1	88.0 (2)	CB1–Sb–CC1	98.6 (3)
O2–Sb–O3	79.6 (2)	Sb–O2–C2	113.8 (4)
O2–Sb–CA1	93.1 (2)	Sb–O3–C3	114.3 (4)
O2–Sb–CB1	162.7 (2)	Sb–Cl–HN	134 (2)
O2–Sb–CC1	91.2 (2)	Cl–HN–N	163 (8)
O3–Sb–CA1	91.4 (2)		

[a] Numbers in parentheses are estimated standard deviations. [b] Atoms are labeled to agree with Figure 3.

the unsubstituted one in the hydrate, is much closer to a TBP. The axial and equatorial angles are 163.0 (2) and 111.4 (2)°, respectively, with angular distortions not along the Berry pseudorotational coordinate. Actually the angular displacements imply an anti-Berry distortion from the ideal TBP.

The accompanying paper[38] supplies an additional derivative, closely related, having a single nitro substituent on the catechol ring, i.e., triphenyl(4-nitrocatecholato)antimony(V). Here, X-ray analysis[38] shows a geometry displaced 68.5% TBP → RP (with unit vectors). Both the nitro derivative and **1** contain electron-withdrawing substituents, a factor that has usually resulted in enhancing structural displacement toward the RP.[4–6,39] Details of the structural analysis of the nitro derivative[38] show that the presence of weakly associated dimeric units accounts for the strong displacement toward the RP. Hence, the unusual feature remaining is the RP form found for the hydrated derivative. The divergence in structural displacements between **1** and the hydrate suggests lattice effects are influential in controlling geometry and that lattice effects are dominant in the hydrate. This assertion becomes more reasonable in the context of the relative ease of distortion of five-coordinated antimony. It is known from dynamic NMR studies on group 5 pentacoordinated compounds[6] that molecular nonrigidity increases in the order P < As < Sb. It is further expected that as the element becomes more metallic and less electronegative a greater tendency for the appearance of lattice effects should arise.[14a]

The ease with which five-coordinated antimony undergoes distortion is reinforced by the geometry found for the triphenylantimony derivative **3**, containing the naphthalenediol ligand. The long Sb–Cl bond may be viewed as inducing a distortion intermediate between five- and six-coordinated structures. The resultant trans basal angles, relative to a RP, are 162.7 (2) and 166.7 (2)°, neither the 180° expected for an octahedron nor the 150° expected for a main-group-element RP. We view this geometrical form to result as a consequence of the high degree of molecular nonrigidity associated with five-coordinated antimony.

The geometry obtained for the stiborane **2**, which contains the same tetrachloro-substituted catecholate as **1** and a triorgano moiety as well, although cyclic instead of acyclic, is near rectangular pyramidal. The latter composition is the first one that meets the requirements found for other five-coordinated derivatives of group 4 and 5 elements favoring the RP structure as described in the Introduction. There has been no example of a compound of these elements that having met these requirements did not have a RP structure.

It might be expected that the presence of the biphenylene ring in **2** is responsible for its near-RP geometry. However, Millington and Sowerby[40] studied triphenyl(2,2′-biphenylene)stibine, $Ph_3Sb(C_{12}H_8)$, and found a TBP structure that is displaced only 15.8% (unit vectors)[18] toward a RP.

The presence of two independent molecules in **2** exhibiting considerable divergence in geometrical displacement attributable to lattice effects emphasizes again the high degree of stereochemical nonrigidity of five-coordinated antimony compounds.

Conclusion. In agreement with additional ramifications explored in the accompanying paper[38] (assuming lattice effects are properly accounted for), a general progression from the TBP toward the RP for pentacoordinated antimony is encountered as the number of acyclic ligands are replaced by unsaturated five-membered rings. The stiborane having the greatest RP character is expected to be associated with the general composition

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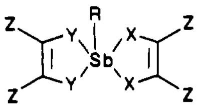
(41) The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)



where X and Y may be the same or different and Z represents an electron-delocalizing element.

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Supplementary Material Available: Thermal parameters, hydrogen atom parameters, additional bond lengths and angles (Tables S1–S3, respectively, for **1**, Tables S4–S6 for **2**, and Tables S7–S9 for **3**), and deviations from least-squares mean planes (Tables S10–S12 for **1–3**, respectively) (23 pages); tables of calculated and observed structure factors for **1–3** (40 pages). Ordering information is given on any current masthead page.

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Distortion Coordinate for Nonrigid Five-Coordinated Antimony. Synthesis and Structure of Oxygen- and Sulfur-Containing Cyclic Organostiboranes[1,2]

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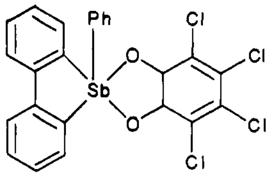
The monocyclic stiboranes $Ph_3Sb[S_2C_2(CN)_2]$ (**1**) and $Ph_3Sb(O_2C_6H_3\text{-}4\text{-}NO_2)$ (**3**) were synthesized by the reaction of Ph_3SbCl_2 with the disodium salt of maleonitriledithiol and by the reaction of 4-nitrocatechol in the presence of Et_3N, respectively. Reaction of *p*-tolylstibonic acid with pinacol gave the bicyclic stiborane $(Me_4C_2O_2)_2Sb(C_6H_4\text{-}p\text{-}Me)$ (**2**). Stiboranes **2** and **3** are new compounds. X-ray analysis revealed that **1** and **2** are trigonal bipyramidal while **3** is closer to a square-pyramidal structure. Molecules of **3** exist in the solid as weakly connected dimers, which accounts for its structural displacement toward the square pyramid. The distortion coordinate expressing solid-state nonrigidity is the Berry pseudorotational coordinate, the same as that found for pentacoordinated structures of other elements of main groups 4 (14) and 5 (15). However, lattice effects enter as a more important structural influence for some stiboranes. Stiborane **1** crystallizes in the monoclinic space group $P2_1/c$ with a = 9.844 (3) Å, b = 10.101 (2) Å, c = 20.537 (4) Å, β = 92.63 (2)°, and Z = 4. **2** crystallizes in the tetragonal space group $I\bar{4}2d$ with a = 23.787 (5) Å, c = 7.070 (1) Å, and Z = 8. **3** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.131 (1) Å, b = 18.945 (5) Å, c = 10.788 (2) Å, β = 99.69 (1)°, and Z = 4. The final conventional unweighted agreement factors were 0.024 (**1**), 0.025 (**2**), and 0.032 (**3**).

Introduction

In the previous paper,[1b] we showed that, in the absence of lattice effects, the formation of the normally higher energy square-pyramidal structure for five-coordinated antimony compounds follows the same general criteria found for other group 4 (14[39])[3-5] and 5 (15[39])[6-8] elements in the pentacoordinated state.

Since lattice effects are more pronounced with antimony as the central element[9] and hence act as a complicating feature compared to the case for phosphorus or arsenic, it remains to establish how well a distortion coordinate between the trigonal bipyramid (TBP) and square or rectangular pyramid (RP) is followed and what influence substituent effects have in controlling structural distortions along this coordinate. For example, it is concluded[1b] that lattice effects are important in leading to the formation of square pyramids for $SbPh_5$[10] and the monohydrate composition $[Ph_3Sb(O_2C_6H_4)]_2\cdot H_2O$.[11] This assertion is supported by the presence of trigonal-bipyramidal geometries in the cyclohexane solvate $SbPh_5\cdot 0.5C_6H_{12}$,[12] the tolyl derivative $(p\text{-}CH_3\text{-}C_6H_4)_5Sb$,[13] and the chlorinated monocyclic $Ph_3Sb(O_2C_6Cl_4)$[1b] analogue to the monohydrate composition above.

Thus far, the square pyramid has been found in only one spirocyclic derivative, $(Cl_4C_6O_2)(C_{12}H_8)SbPh\cdot 0.25C_6H_6\cdot 0.25CH_2Cl_2$.[1b]



Ring unsaturation is present, and like atoms are bound to antimony in each of the rings, a criterion found in forming square pyramids for phosphoranes[6,7] and arsoranes,[8] as well as five-coordinated anionic silicates,[3] germanates,[4] and stannates[5] isoelectronic with the group 5 elements.

It is necessary to explore a greater variety of stiboranes to define the form of the distortion coordinate for hypervalent antimony in the pentacoordinated state. With the realization that stiboranes are more fluxional or nonrigid entities than their phosphorus and

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(1) (a) Pentacoordinated Molecules. 68. (b) Part 67: Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.*, preceding paper in this issue.

(2) Presented in part at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; paper INOR 196.

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