Syntheses, Structures, and Equilibria of *o*-, *m*-, *p*-Tolyl- and Phenylantimony Rings ☆

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Received December 9, 1994

Key Words: Cyclopentastibanes / Cyclohexastibanes / Antimony compounds / Phenylantimony rings

Exchange reactions of R_3Sb (R = *o*-Tol, *m*-Tol, *p*-Tol) with $SbCl_3$ in a 1:2 molar ratio give $RSbCl_2$. Silylstibanes $RSb(SiMe_3)_2$ were obtained by reaction of $RSbCl_2$ and Me_3SiCl with Mg in THF. Slow access of air to solutions of $RSb(SiMe_3)_2$ afforded orange crystals of the composition $(RSb)_n$. Crystal structures were determined by X-ray crystallography for R = o-Tol and *m*-Tol as stacks of $(RSb)_6$ rings in the chair conformation with equatorial substituents. In the crystals of $(m\text{-TolSb})_6$ there are short intermolecular Sb···Sb distances of 420 pm. Solutions of $(RSb)_n$ (R = Ph, *o*-Tol, *m*-Tol, *p*-Tol) in C_6D_6 were analyzed by ^{1}H-NMR spectroscopy. They contain $(RSb)_5$ and $(RSb)_4$ in equilibria. Raman spectra of $(PhSb)_6$ or $(p\text{-TolSb})_n$ show signals for Sb_n at $\tilde{\nu}$ = 151 or 153 cm^{-1}. ^{13}C-CP-MAS-NMR data of $(p\text{-TolSb})_n$ are reported.

An intriguing aspect of the chemistry of those organoantimony rings $(RSb)_n$ that are not protected by bulky substituents is the readiness to take part in ring-ring equilibria[1]. In such labile systems the ring size may be different in the solid state and in solution and should be determined in both phases. Known ring systems have been precisely defined only in the solid state, e.g. $(PhSb)_6$[2,3], or only in solution, e.g. $(EtSb)_{4,5}$[4], because the characterization in other phases was hindered for chemical or analytical reasons. In searching for organoantimony ring systems that can be characterized both in solution and in the solid state, we chose the tolylantimony system and report here on the multistep syntheses of *o*-, *m*-, and *p*-tolylantimony and on the results of NMR and X-Ray studies demonstrating the presence of pentamers and tetramers in solution and of hexamers in the solid state. In this context solutions of phenylantimony were also reexamined. Raman spectra and ^{13}C-CP-MAS-NMR (CP-MAS: cross polarization – magic angle spinning) spectroscopy were employed for the characterization of crystals of phenyl- and *p*-tolylantimony. For preliminary communications see refs.[5,6].

Syntheses, Properties, and Structures of $(RSb)_n$ (R = *o*-Tol, *m*-Tol, *p*-Tol)

The syntheses of the tolylantimony ring compounds have been achieved by multistep reactions analogous to the syntheses of phenylantimony[2,3]. The preparations start with the exchange reactions of $SbCl_3$ and the respective tritolylstibanes in the absence of solvent giving $RSbCl_2$ (R = *o*-Tol, *m*-tol, *p*-Tol) in almost quantitative yields as white crystalline solids. Addition of solutions of $RSbCl_2$ in THF to magnesium filings and Me_3SiCl in the same solvent gave $MgCl_2$ and $RSb(SiMe_3)_2$. The novel tolylbis(trimethylsilyl)-stibanes are light yellow air sensitive liquids. They ignite spontaneously when they are exposed to the atmosphere on paper. When, however, the access of air to solutions in THF or other solvents (e.g. toluene, mesitylene, 1,4-dioxane, DMF) is very slow, orange crystals of *o*-, *m*-, or *p*-tolylantimony form.

$$R_3Sb + 2\ SbCl_3 \rightarrow 3\ RSbCl_2$$
$$RSbCl_2 + 2\ Mg + 2\ Me_3SiCl \rightarrow RSb(SiMe_3)_2 + 2\ MgCl_2$$
$$RSb(SiMe_3)_2 + 1/2\ O_2 \rightarrow 1/n\ (RSb)_n + (Me_3Si)_2O$$
$$R = o\text{-Tol}, m\text{-Tol}, p\text{-Tol}$$

The novel rings are stable in the air only as crystals. They react in solution with traces of air to give white solids of the approximate composition $(RSbO)_x$. The color of the solutions is yellow. The solid antimony rings were obtained in 20–60% yield. Soluble side products remaining in the initial reaction solution include compounds of the type R_3Sb, $R_2SbOSiMe_3$, R_4Sb_2, and R_4Sb_2O.

The structures of *o*- and *m*-tolylantimony in the crystalline state were determined by X-ray diffraction as centrosymmetric $(RSb)_6$ rings in the chair conformation with equatorial substituents (Figures 1 and 2). In the crystal, the antimony six-membered rings are packed to form parallel stacks (Figures 3 and 4). In the stacks of $(m\text{-TolSb})_6$ there are intermolecular Sb···Sb contacts of 420 pm. Close contacts between *o*-tolylantimony rings are not observed. This may be a consequence of a better shielding of the antimony atoms and indicates that intermolecular interactions are not essential for the stabilization of antimony six-membered rings in the crystal. Both structures compare very well with the arrangement of rings in the crystals of $(PhSb)_6 \cdot$ benzene or other solvates of the phenylantimony hexamer. The crystals of *p*-tolylantimony were not suitable for X-ray analyses and were therefore characterized by other methods. For example, the ^{13}C-CP-MAS-NMR spectrum shows

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one set of signals for the *p*-tolyl groups as expected for (*p*-TolSb)$_6$ or other symmetric rings.

Figure 1. Molecular structure of (*o*-TolSb)$_6$ in the crystal, distances: Sb–Sb 281.8–283.6(1), Sb–C 217.6–219.0(12) pm; bond angles Sb–Sb–Sb 85.5–99.4(1), Sb–Sb–C 91.1–100.3(3)°, torsion angles SbSb–SbSb 80.6–91.2(1), SbSb–SbC 167.6–177.2(3)°

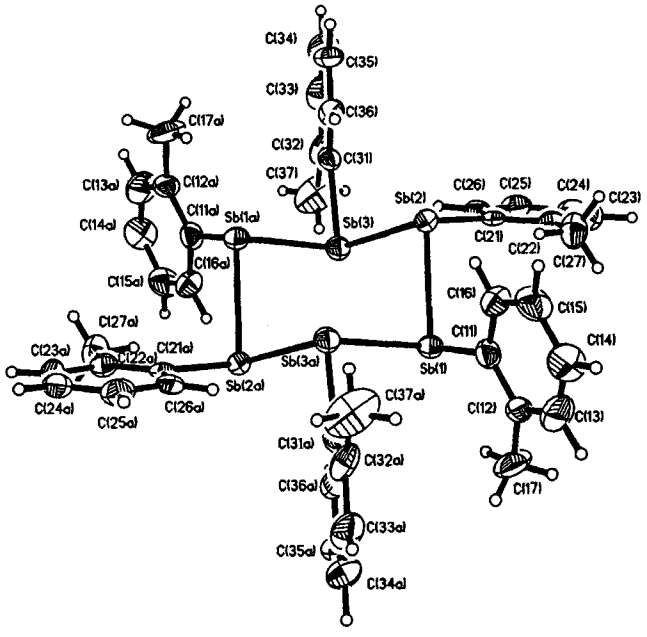
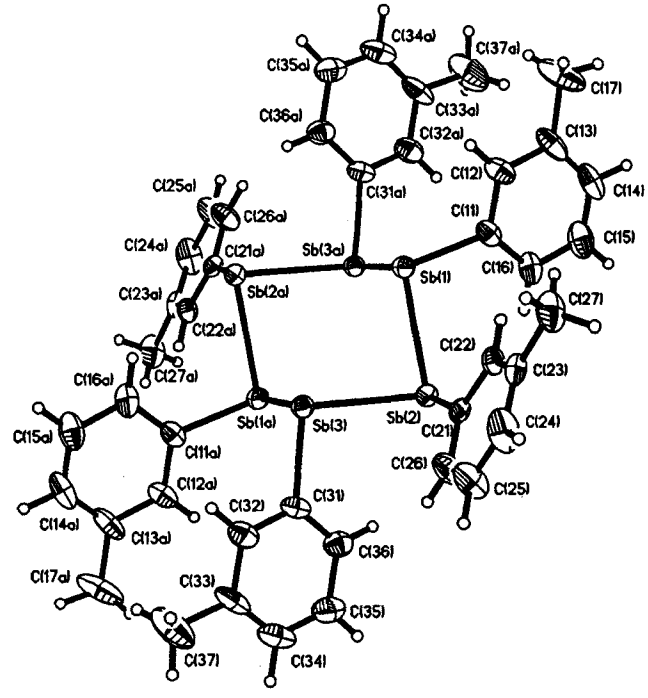


Figure 2. Molecular structure of (*m*-TolSb)$_6$ in the crystal, distances: Sb–Sb 282.8–283.4(1), Sb–C 215.6–218.1(9) pm; bond angles Sb–Sb–Sb 83.2–96.0(1), Sb–Sb–C 89.8–99.6(3)°, torsion angles SbSb–SbSb 84.2–88.9(1), SbSb–SbC 174.8–179.3(3)°



The size and the structure of the tolylantimony rings in solution were determined by ^{1}H-NMR spetroscopy. There are four singlet signals in the region of the methyl protons that have their counterparts in the multiplets of the aryl

Figure 3. Crystal structure of (*o*-TolSb)$_6$, projection of the *xz* plane

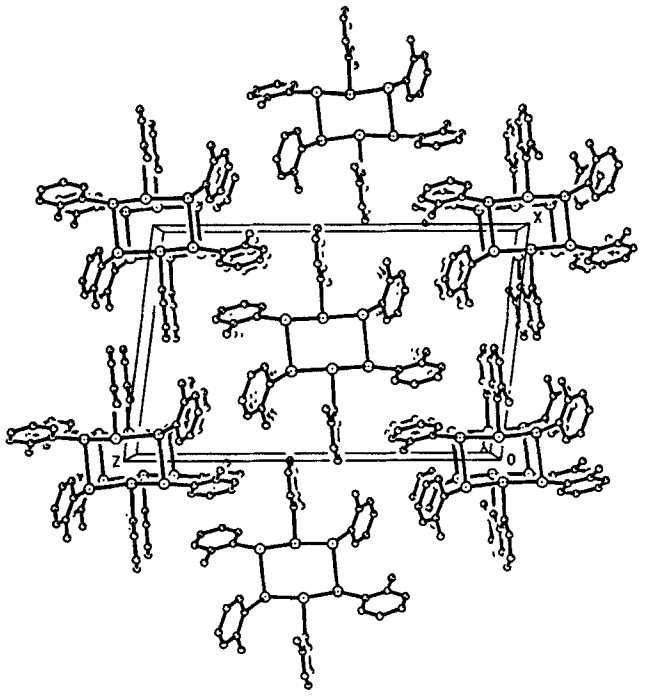
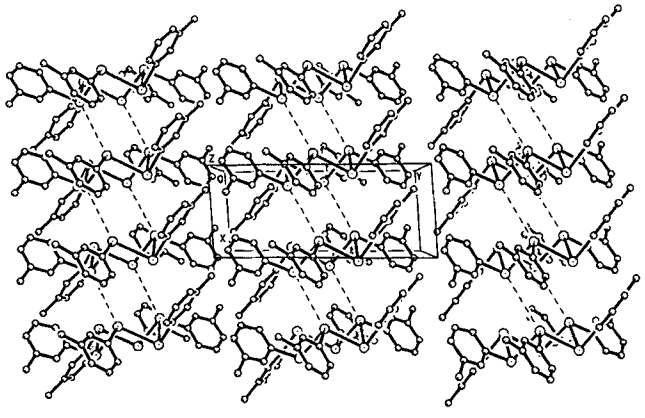


Figure 4. Crystal structure of (*m*-TolSb)$_6$, projection of the *xy* plane, intermolecular distance Sb---Sb 420 pm



protons. The assignment of these signals is based on spectra at various concentrations. Three groups of signals maintain their relative ratio of intensities of 2:2:1 on dilution whereas the intensity of the fourth group increases. The ^{1}H-NMR spectra of the *o*- and *p*-tolylantimony rings in solution show the same pattern for the methyl groups, and in all cases the signals of the aryl protons correspond to the distribution of the methyl signals. Based on these spectroscopic results the presence of hexamers in solution must be excluded. The 2:2:1 sets of signals indicate the presence of pentamers (RSb)$_5$ where the tolyl groups adopt a maximum of *trans* positions and the rings have a time-equalized plane of symmetry due to an equilibration of conformations on the NMR time scale. 2:2:1 distributions are also observed in the spectra of the alkylantimony five-membered rings[4] or five-membered organoarsenic[1] or organophosphorus[7] cycles.

The fourth methyl singlet signals and the related aryl signals in the spectra of the tolylantimony rings correspond to four-membered cycles with equivalent substituents in the *all-trans* configuration. This assignment is based on the observed increase of the intensities of the signals of $(RSb)_4$ relative to the signals of $(RSb)_5$ as expected for ring-ring equilibria following the principle of Le Chatelier. On dilution the number of small rings increases at the expense of larger rings and vice versa. In saturated solutions at room temperature the molar ratio of $(RSb)_5$ to $(RSb)_4$ is approximately 8:2. The following equations summarize the equilibria found in the tolyl antimony ring systems in the solid state and in solution:

$$1/6\ (RSb)_6 \rightleftharpoons 1/5\ (RSb)_5 \rightleftharpoons 1/4\ (RSb)_4$$

(R = *o*-Tol, *m*-Tol, *p*-Tol)

The search for signals of trimers in solution even at very low concentrations was not successful. Trimers are however the most abundant species in the gas phase as suggested by mass spectrometry. Mass spectra also contain signals of pentamers and tetramers and therefore the question arises if the trimers are individual species or fragments of larger oligomers. Experiments with varied electron energy show that the intensities of the signals of the trimers are independent of the signals of tetramers and pentamers, and hence the ions $R_3Sb_3^+$ may be considered as molecular ions rather than as fragments.

^{1}H-NMR Spectra of Phenylantimony Rings in Solution

After the analyses of the tolylantimony rings the phenylantimony system was reexamined. A careful analysis of the complicated ^{1}H-NMR spectra of solutions obtained form crystals of $(PhSb)_6 \cdot C_6H_6$ indeed revealed the 2:2:1 ratio of multiplets that are typical of the five-membered ring $(PhSb)_5$ and a set of signals with increasing intensity on dilution which correspond to $(PhSb)_4$. These findings prove that equilibria between solid hexamers and pentamers and tetramers in solution are also characteristic of phenylantimony rings.

$$1/6\ (PhSb)_6 \rightleftharpoons 1/5\ (PhSb)_5 \rightleftharpoons 1/4\ (PhSb)_4$$

Raman Spectra of Crystals of Phenylantimony and *p*-Tolylantimony

The Raman spectra of solid $(PhSb)_6 \cdot C_6H_6$ and solid $(p\text{-TolSb})_n$ were recorded in an attempt to determine the ring size of *p*-tolylantimony by comparison with the lines of the respective antimony ring skeletons. For a Sb_6 ring in the chair conformation with D_{3d} symmetry, four Raman-active vibrations (2 A_{1g}, 2 E_g) are expected. The most intensive line should result from a A_{1g} ring stretching mode. In the spectrum of $(PhSb)_6 \cdot C_6H_6$ two signals can be assigned to vibrations of the Sb_6 skeleton. The line at 151 cm^{-1} is assigned to the A_{1g} stretch of the Sb_6 ring because it is the most intensitve signal in the spectrum and the position is similar to the Sb–Sb stretching vibrations reported for $MeC(CH_2Sb)_3$ (210–150 cm^{-1})[8] and for $Ph_2SbSbPh_2$ (141 cm^{-1})[9]. In the Raman spectrum of $(Ph_2Sn)_6$ and other cyclohexatin compounds adopting the chair conformation there is an intense band at 150 cm^{-1}[10]. The band at 77 cm^{-1} may result from ring deformations. All the other signals observed in the spectrum of $(PhSb)_6$ correspond to lines in the spectrum of tetraphenyldistibane. They are assigned to the vibrations of the PhSb units. In the Raman spectrum of $(p\text{-TolSb})_n$ there are three signals in the region of the vibrations of the antimony rings. The most intensive signal is observed at 153 cm^{-1}. It corresponds to a Sb_6 ring stretching vibration but is too broad to unambiguously demonstrate the exclusive presence of hexamers in the crystals of *p*-tolylantimony.

Discussion

The equilibria observed in the phenyl- and tolylantimony ring systems in solution correspond to the behavior of alkylantimony rings with slim alkyl substituents. In all these systems pentameric rings dominate over tetrameric species in solution. Trimeric ions occur in the mass spectra. Interesting differences emerge however in the absence of a solvent. Yellow crystals of hexamers are formed in the case of the arylantimony system whereas polymers or large rings are obtained as black powders or films when the solvent is removed from solutions of alkylantimony rings[4]. Arylantimony polymers are known. They are formed by dehalogenation of arylantimony dihalides or by action of reactive halogen compounds on arylantimony rings. Advantages of the silylstibane method for the syntheses of rings lie in the absence of halides, which may act as initiators for polymerization reactions and in the formation of crystals directly from the reaction mixture. Another aspect of the stabilization of arylantimony rings is the efficient packing not only of the Sb_6 rings but also of the aryl substituents in the solid state. The facile changes of ring size in solution require efficient mechanisms. Following the proposal made by Baudler[11] for ring-ring interconversions between alkylphosphorus homocycles, we assume a sequence of intermolecular and transannular four-center metatheses reactions between antimony atoms. For phenyl- and tolylantimony rings, this process is fast at room temperature and allows thermodynamic control of the ring size. Kinetic control is typical of organoantimony rings with bulky substituents and for organoarsenic and organophosphorus rings. This appears to be the major difference between these homocycles.

We thank Mrs. *W. Buß* and Prof. Dr. *R. Minkwitz*, University of Dortmund, for recording Raman spectra, Prof. Dr. *B. Wrackmeyer*, University of Bayreuth, for measuring the ^{13}C-CP-MAS spectrum, Dr. *R. Kaller* for experimental contributions to the synthesis of $(p\text{-TolSb})_5$, and we gratefully acknowledge financial support by the *Fonds der Chemischen Industrie*.

Experimental

Except for the last step in the ring synthesis all manipulations were carried out in an Ar atmosphere in carefully dried solvents. – ^{1}H NMR: Bruker WH 360. – ^{13}C-CP-MAS NMR: Bruker MSL 300. – MS: Finnigan MAT 8222. The pattern of antimony-containing ions was compared with theoretical values. – Raman: Co-

derg T 800 (Spectra Physics Kr^+ Laser 2016). – Elemental analyses: Beller Mikroanalytisches Laboratorium, Göttingen. – *o*-Tol_3Sb[12], *p*-Tol_3Sb[13,14], *p*-$TolSbCl_2$[15], and $(PhSb)_6 \cdot C_6H_6$[3] were prepared according to procedures reported in the literature and characterized by spectroscopic methods. – *o-Tol$_3$Sb:* ^1H NMR ($CDCl_3$): δ = 2.49 (s, 3H, CH_3), 6.95–7.05, 7.25–7.30 (m, 4H, C_6H_4). – ^1H NMR (C_6D_6): δ = 2.39 (s, 3H, CH_3), 6.82–6.88, 7.01–7.11, 7.29, 7.31 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 394 (60) [M^+], 303 (27) [R_2Sb], 212 (25) [RSb], 182 (85) [R_2], 91 (100) [R = C_7H_7]. – *p-Tol$_3$Sb:* ^1H NMR ($CDCl_3$): δ = 2.35 (s, 3H, CH_3), 7.11–7.19, 7.30–7.36 (AA'XX' spin system, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 394 (60) [M^+], 303 (20) [R_2Sb], 212 (100) [RSb], 182 (90) [R_2], 91 (82) [R = C_7H_7]. – *p-TolSbCl$_2$:* ^1H NMR (C_6D_6): δ = 2.00 (s, 3H, CH_3), 6.89–6.95, 7.38–7.41 (AA'XX' spin system, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 282 (55) [M^+], 247 (30) [RSbCl], 182 (18) [R_2], 91 (100) [R = C_7H_7].

X-Ray Crystal Structure Determinations[16]: Diffractometer Siemens P4, Mo-K_α radiation, graphite monochromator, T = 173 K, 2Θ-ω scans, 3 reference reflections (every 197 reflections); solution and refinement by direct methods, full-matrix least-squares (Sb and C anisotropic, H atoms: fixed with isotropic temperature factors on calculated positions), system used: Siemens SHELXTL PLUS (VMS)[17], absorption correction with program DIFABS[18].

(o-TolSb)$_6$: $C_{42}H_{42}Sb_6$ (1277.3); monoclinic space group $P2_1/n$, a = 1342.1(3), b = 736.2(2), c = 2152.2(4) pm, β = 97.42(3)°, V = 2108.5(8) $pm^3 \cdot 10^6$, Z = 2, D_c = 2.012 $g \cdot cm^{-3}$, μ(Mo-K_α) = 3.816 mm^{-1}. 5350 reflections measured (Θ_{max} = 25°), 3698 independent reflections (R_{int} = 2.20%), R = 4.28% [calculated for 2153 reflections with $F > 4\sigma(F)$ for 219 parameters]. wRT = 4.91%, weighting scheme: $w^{-1} = \sigma^2(F) + 0.0020\,F^2$.

(m-TolSb)$_6$: $C_{42}H_{42}Sb_6$ (1277.3); triclinic space group $P\bar{1}$, a = 543.7(2), b = 1333.3(3), c = 1451.8(3) pm, α = 80.58(3), β = 98.26(3), γ = 86.18(3)°, V = 1036.0(5) $pm^3 \cdot 10^6$, Z = 1, D_c = 2.047 $g \cdot cm^{-3}$, μ(Mo-K_α) = 3.883 mm^{-1}. 5318 reflections measured (Θ_{max} = 27.5°), 4725 independent reflections (R_{int} = 1.26%), R = 4.91% [calculated for 3203 reflections with $F > 6\sigma(F)$] for 219 parameters]. wR = 5.89%, weighting scheme: $w^{-1} = \sigma^2(F) + 0.0004\,F^2$.

Tri-m-tolylantimony: A solution of 22.5 g (0.0985 mol) of $SbCl_3$ in 100 ml of diethyl ether was added dropwise to a Grignard solution prepared from 51.3 g (0.3 mol) of 3-$CH_3C_6H_4Br$ and 8 g (0.33 mol) of Mg in 500 ml of THF. The mixture was stirred at room temp. for 16 h, and 200 ml of water was added. The ether layer was separated and dried with Na_2SO_4. After removal of the solvent at reduced pressure *m*-Tol_3Sb was obtained as a white solid in a yield of 18.05 g (46%). The product was used without further purification. – ^1H NMR ($CDCl_3$): δ = 2.31 (s, 3H, CH_3), 7.12–7.16, 7.20–7.22, 7.31 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 394 (46) [M^+], 303 (10) [R_2Sb], 212 (100) [RSb], 182 (39) [R_2], 91 (56) [R = C_7H_7] {ref.[19] *m/z* (%): 394 (18.6) [M^+]}.

o-Tolylantimony Dichloride: A mixture of 8.50 g (0.037 mol) of freshly sublimed antimony trichloride and 7.37 g (0.019 mol) tri-*o*-tolylantimony was stirred at 90°C for 2 h. After cooling of the mixture the white solid of *o*-$TolSbCl_2$ was obtained in quantitative yield. – ^1H NMR (C_6D_6): δ = 1.98 (s, 3H, CH_3), 6.76–6.79, 6.95–7.10, 8.08–8.11 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 282 (53) [M^+], 247 (27) [RSbCl], 212 (3) [RSb], 91 (100) [R = C_7H_7]. – $C_7H_7Cl_2Sb$ (283.8): calcd. C 29.63, H 2.49; found C 28.61, H 2.65.

m-Tolylantimony Dichloride: A mixture of 8.51 g (0.037 mol) of freshly sublimed antimony trichloride and 7.4 g (0.019 mol) tri-*m*-tolylantimony was stirred at 90°C for 2 h. After cooling light yellow solid *m*-$TolSbCl_2$ was obtained in quantitative yield. – ^1H NMR (C_6D_6): δ = 1.98 (s, 3H, CH_3), 6.82–6.90, 6.95–7.10, 7.25–7.40 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 282 (59) [M^+], 247 (30) [RSbCl], 212 (10) [RSb], 182 (35) R_2, 91 (100) [R = C_7H_7]. – $C_7H_7Cl_2Sb$ (283.8): calcd. C 29.63, H 2.49; found C 29.87, H 2.78.

o-Tolylbis(trimethylsilyl)antimony: A solution of 4.62 g (0.016 mol) of *o*-$TolSbCl_2$ in 60 ml of THF was added dropwise to a mixture of 0.85 g (0.035 mol) of Mg and 3.80 g (0.035 mol) of Me_3SiCl in 120 ml of THF. After stirring at room temp. for 12 h the solvent was removed, and the residue was extracted twice with 50 ml of petroleum ether. The combined extracts were separated through a frit from black solids. Evaporation of the petroleum ether gave 3.6 g (63.0%) of *o*-$TolSb(SiMe_3)_2$ as a yellow, air- and light-sensitive liquid. – ^1H NMR (C_6D_6): δ = 0.36 (s, 18H, Me_3Si), 2.50 (s, 3H, *o*-CH_3), 6.85–6.91, 7.00–7.09, 7.52–7.56 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 358 (11) [M^+], 343 (3) [$M^+ - CH_3$], 285 (1) [$RSbSiMe_3$], 207 (22) [$SbSi_2Me_2$], 149 (94) [SbSi], 121 (12) [Sb], 91 (20) [R = C_7H_7], 73 (100) [Me_3Si]. – $C_{13}H_{25}SbSi_2$ (359.3): calcd. C 43.46, H 7.01; found C 43.64, H 6.76.

m-Tolylbis(trimethylsilyl)antimony: The reaction of 4.62 g (0.016 mol) of *m*-$TolSbCl_2$ with 0.85 g (0.035 mol) of Mg and 3.80 g (0.035 mol) of Me_3SiCl was carried out as described above and gave 3.5 g (62.0%) of *m*-$TolSb(SiMe_3)_2$ as a yellow, air- and light-sensitive liquid. – ^1H NMR (C_6D_6): δ = 0.36 (s, 18H, Me_3Si), 2.10 (s, 3H, *m*-CH_3), 6.8–7.1, 7.3–7.5 (m, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 358 (1) [M^+], 285 (19) [$RSbSiMe_3$], 270 (10) [$RSbSiMe_2$], 227 (100) [RSbMe], 212 (68) [RSb], 207 (35) [$SbSi_2Me_2$], 182 (64) [R_2], 149 (20) [SbSi], 91 (78) [R], 73 (28) [Me_3Si], R = C_7H_7. – $C_{13}H_{25}SbSi_2$ (359.3): calcd. C 43.46, H 7.01; found C 44.93, H 7.26.

p-Tolylbis(trimethylsilyl)antimony: The reaction of 4.62 g (0.016 mol) of *p*-$TolSbCl_2$ with 0.85 g (0.035 mol) of Mg and 3.80 g (0.035 mol) of Me_3SiCl was carried out as described above and gave 3.9 g (67.0%) of *p*-$TolSb(SiMe_3)_2$ as a yellow air- and light-sensitive liquid. A solution of 9.24 g (0.326 mol) of *p*-$TolSbCl_2$ in 120 ml of THF was added dropwise to a mixture of 1.7 g (0.07 mol) of Mg and 7.60 g (0.07 mol) of Me_3SiCl in 120 ml of THF. After stirring at room temp. for 12 h the solvent was removed, and the residue was extracted twice with 120 ml of petroleum ether. The combined extracts were separated through a frit from black solids. Evaporation of the petroleum ether gave 3.9 g (67%) of *p*-$TolSb(SiMe_3)_2$ as a yellow air- and light-sensitive liquid. – ^1H NMR (C_6D_6): δ = 0.36 (s, 18H, Me_3Si), 2.08 (s, 3H, *p*-CH_3), 6.85–6.91, 7.53–7.59 (AA'XX' spin system, 4H, C_6H_4). – MS (70 eV), *m/z* (%): 358 (9) [M^+], 343 (1) [M^+ – Me], 212 (68) [RSb], 207 (29) [$SbSi_2Me_2$], 149 (100) [SbSi], 91 (5) [R], 73 (90) [Me_3Si], R = C_7H_7. – $C_{13}H_{25}SbSi_2$ (359.3): calcd. C 43.46, H 7.01; found C 45.67, H 7.03.

o-Tolylantimony: A solution of 0.06 g (0.17 mmol) of *o*-$TolSb(SiMe_3)_2$ in 1.5 ml of THF was placed in a glass tube that was not perfectly closed with a plastic cap (5-mm NMR tube). After several days the solution became colorless, and 0.011 g (23%) of orange needles of $(o\text{-TolSb})_n$ (m.p. 170°C) formed. The crystals were separated mechanically and washed with petroleum ether. It is useful to perform this reaction in parallel experiments. – ^1H NMR (C_6D_6), δ = 2.03 (s, 6H, CH_3), 2.10 (s, 3H, CH_3), 2.29 (s, 6H, CH_3), 6.8–7.1, 7.8–8.0, 8.5–8.6 (m, 20H, C_6H_4) *(o-TolSb)$_5$*; 2.12 (s, 3H, CH_3), 8.2–8.4 (m, 4H, C_6H_4) *(o-TolSb)$_4$*. – MS (70 eV), *m/z* (%): 848 (1) [R_4Sb_4], 757 (1) [R_3Sb_4], 636 (64) [R_3Sb_3], 454 (3) [RSb_3], 212 (100) [RSb], R = C_7H_7. – $C_{42}H_{42}Sb_6$ (1277.3): calcd. C 39.50, H 3.31; found C 40.44, H 3.32.

m-Tolylantimony: The reaction of 0.17 g (0.47 mmol) of *m*-$TolSb(SiMe_3)_2$ in 1.5 ml of THF with air was carried out as described above, and 0.031 g (66%) of orange needles of $(m\text{-TolSb})_6$

(m.p. 165°C) formed. – ^{1}H NMR (C_6D_6), δ = 1.97 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 2.07 (s, 3H, CH_3), 6.8–7.1, 7.2–8.0 (m, 20H, C_6H_4) (*m*-TolSb)$_5$; 2.03 (s, 3H, CH_3), 6.8–8.0 (m, 4H, C_6H_4) *(m-TolSb)$_4$*. – MS (70 eV), *m/z* (%): 1060 (1) [R_5Sb_5], 848 (3) [R_4Sb_4], 757 (3) [R_3Sb_4], 636 (25) [R_3Sb_3], 454 (1) [RSb_3], 212 (72) [RSb], 182 (80) [R_2], 91 (100) [R = C_7H_7]. – $C_{42}H_{42}Sb_6$ (1277.3): calcd. C 39.50, H 3.31; found C 37.84, H 3.93.

p-Tolylantimony: The reaction of 0.092 g (0.255 mmol) of *p*-TolSb($SiMe_3$)$_2$ in 1.5 ml of THF with air was carried out as described above, and 0.06 g (26%) of yellow crystals of (*p*-TolSb)$_n$ (m.p. 170°C) formed. – ^{1}H NMR (C_6D_6), δ = 2.03 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 2.08 (s, 3H, CH_3), 6.80–6.85, 6.88–6.91, 6.92–6.93 (AA'XX' spin systems, 20H, C_6H_4) *(p-TolSb)$_5$*; 2.07 (s, 3H, CH_3), 6.90–6.95, 7.75–7.79 (m, 4H, C_6H_4) *(p-TolSb)$_4$*. – ^{13}C-CP-MAS NMR: 21.4 (CH_3), 130.0 (C_6H_4), 138.7 (C_6H_4). – MS (70 eV), *m/z* (%): 1060 (1) [R_5Sb_5], 848 (1) [R_4Sb_4], 757 (1) [R_3Sb_4], 636 (64) [R_3Sb_3], 454 (3) [RSb_3], 212 (25) [RSb], 182 (70) [R_2], 91 (100) [R = C_7H_7]. – Raman: pure solid substance (rel. Int.), $\tilde{\nu}$ = 790 cm^{-1} (1), 294 (1), 229 (1), 212 (1), 181 (5), 153 (10) [νSb–Sb], 70 (5). – $C_{42}H_{42}Sb_6$ (1277.3): calcd. C 39.50, H 3.31; found C 39.32, H 4.36.

Phenylantimony: ^{1}H NMR (C_6D_6), δ = 6.8–7.2 (15H), 7.4–7.5 (4H), 7.85–7.90 (2H), 7.91–7.95 (4H), (m, C_6H_5) *(PhSb)$_5$*; 6.7–7.1, 7.73–7.77 (m, C_6H_5) *(PhSb)$_4$*. – Raman: pure solid substance (rel. int.), $\tilde{\nu}$ = 997 cm^{-1} (2), 649 (1) [r mode], 244 (1) [t mode], 195 (1) [u mode], 183 (1), 174 (1) [x mode], 151 (10) [νSb_6], 77 (4) [δSb_6], $(PhSb)_6$. For the assignments of modes of the phenyl groups see ref.[20].

☆ Dedicated to Prof. Dr. *H. Schumann* on the occasion of his 60th birthday.

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