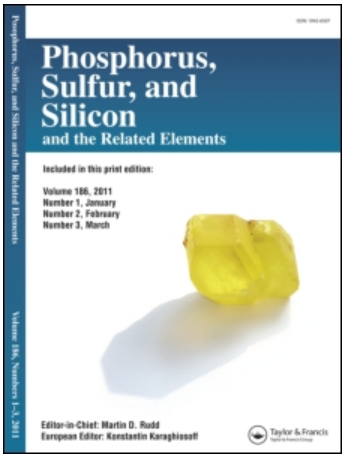

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Novel Organo Antimony Homo and Hetero Cycles

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NOVEL ORGANO ANTIMONY HOMO AND HETERO CYCLES

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Abstract New syntheses and structures of the homocycles $(RSb)_5$ (R = Ph, o-Tol, m-Tol, p-Tol, Me_3SiCH_2), $(RSb)_4[W(CO)_5]_2$ and of the heterocycles $[(Me_3Si)_2CHSbE]_n$ (n = 3,4: E = O,S, Se) are described.

INTRODUCTION

After the syntheses of phenyl[1], p-tolyl[2] and various alkyl antimony homocycles[3] of the type $(RSb)_n$ we became interested in rings with the o-tolyl, m-tolyl or trimethylsilylmethyl substituents and began also to study the coordination properties of antimony rings. We report here on new syntheses of organo antimony homocycles and on the stabilization of heterocycles of the type $(RSbE)_n$ (E = O, S, Se) with the bulky bis(trimethylsilyl)methyl group.

NEW SYNTHESES AND NMR SPECTRA OF $(RSb)_n$ (R = Ph, Tol, Me_3SiCH_2)

The known rings $(RSb)_n$ (R = Ph[1], p-Tol[2]) are formed by the new method described in Eq. (1). They are identified in solution by NMR spectroscopy as pentamers. Phenylantimony is however a hexamer[1] in the solid state. The syntheses of the novel rings $(m\text{-TolSb})_n$ (1) and $(o\text{-TolSb})_n$ (2) have been achieved by the oxidation reaction of Equ. (2). 1 and 2 are yellow crystalline compounds of low solubility in organic solvents. Reaction (3) gives $(Me_3SiCH_2Sb)_n$ (3) in 20 % yield as red crystals. Solutions of 3 are yellow.

$$3\ RSbCl_2 + 2Cp_2Co \longrightarrow 1/n\ (RSb)_n + 2\ Cp_2Co[RSbCl_3] \quad (1)$$
R = Ph, p-Tol, o-Tol

$$RSb(SiMe_3)_2 + 1/2\ O_2 \longrightarrow 1/n\ (RSb)_n + (Me_3Si)_2O \quad (2)$$
R = o-Tol, m-Tol

$$Me_3SiCH_2SbCl_2 + Mg \longrightarrow 1/n\,(Me_3SiCH_2Sb)_n + MgCl_2 \qquad (3)$$

Elemental analyses and mass spectra [1: 70 eV, 190 C m/z (rel. int. %) 852 (2) $R_4Sb_4^+$, 638 (30) R_3Sb_3, 212 (70) RSb, 91 (100) R = C_7H_7; 2: (70eV, 180°C) m/z (%) 852 (1), 638 (20), 212 (40), 91 (100). 3: 70 eV, 220 °C, 834 (2) $R_4Sb_4^+$, 626 (30) R_3Sb_3, 207 (30) RSb, R = Me_3SiCH_2] confirm the identity of 1 - 3. The ^{1}H-NMR spectra in C_6D_6 contain three groups of signals in a 2:2:1 ratio of intensities for each type of equivalent protons. Here only the singlet signals of the methyl groups are given: δ 1, 1,97 [6H], 2,02 [6H], 2,07 [3H]; 2, 2,03 [6H], 2,10 [3H], 2,28 [6H]; 3, 0,17 [18H], 0,18 [9H], 0,19 [18H]. These patterns are characteristic for five membered rings with the substituents in a maximum of trans positions (Figure 1).

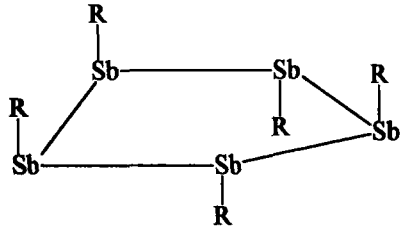

FIGURE 1 Structure of 1 - 3 in solution

The X-Ray crystal structure analyses of 1 and 2 revealed the presence of hexamers in the solid state (Figures 2 and 3).

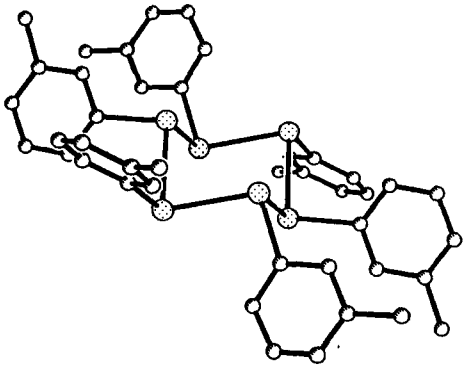

FIGURE 2 Crystal structure of (m-TolSb)$_6$ (1)

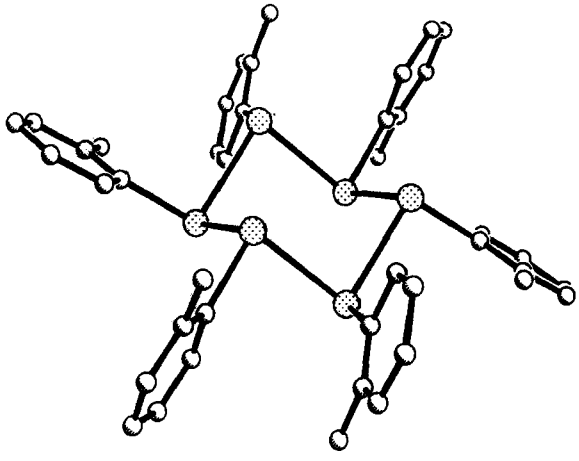

FIGURE 3 Crystal structure of $(o\text{-TolSb})_6$ (2)

The sixmembered antimony rings adopt the chair conformation with the tolyl groups in equatorial positions. The mean Sb-Sb distances are 283 pm for 1 and 2. The angles around the antimony atoms are close to 90°

PENTACARBONYLTUNGSTEN COMPLEXES WITH $(tBuSb)_4$ AS LIGAND

The ligand exchange reaction (4) gives $(tBuSb)_4[W(CO)_5]_2$ (4) in 30% yield as orange crystals of the correct elemental composition.

$$2\ W(CO)_5THF + (tBuSb)_4 \longrightarrow (tBuSb)_4[W(CO)_5]_2 + 2\ THF \quad (4)$$

The mass spectrum (70 eV, 180°C) contains the fragment $(C_4H_9)_3Sb_4W(CO)_5$ [m/z = 977(3)] as signal of highest mass. The ^{1}H-NMR spectra in C_6D_6 show two singlet signals of equal intensity for the different types of tBu groups at δ = 1,42 and δ = 1,49. The crystal structure of 4 (Figure 4) has been determined by X-Ray diffraction. The geometry of the ligand in 4 is very similar to the structure of the free ring. The $W(CO)_5$ units are bent towards the periphery of the ring system.

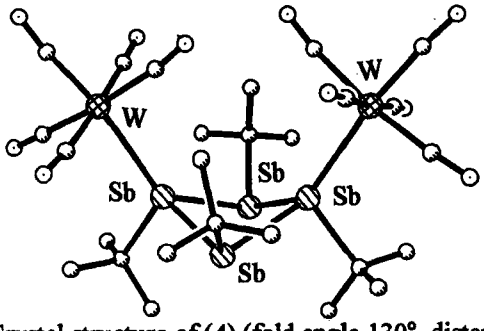

FIGURE 4: Crystal structure of (4) (fold angle 130°, distances Sb-Sb 283 pm, Sb-W 285 pm angles SbSbW 126-135°, SbSbSb 84-85°

HETEROCYCLES OF THE TYPE $(RSbE)_n$ (R = $(Me_3Si)_2CH$, E = O, S, Se)

The heterocycles $(RSbO)_n$ (5), $(RSbS)_n$ (6), $(RSbSe)_n$ (7) (R = $(Me_3Si)_2CH$) are formed in 80 - 90 % yield by the reactions of $(Me_3Si)_2CHSbCl_2$ with NaOH or NaSH in water/ethanol or with Na_2Se in liqu. NH_3. The identity of **5** (colourless crystals), **6** (yellow crystals), and **7** (orange solid) is confirmed by elemental analyses and mass spectra. **5**: MS (70 eV, 160°C) m/z (rel. int.) 1030 (1) $R_2Sb_4O_4$, 891 (1) $R_3Sb_3O_3$, 731 (30) $R_2Sb_3O_3$; **6**: MS (DCI, NH_3) m/z (rel. int.) 1093 (10) $R_3Sb_4S_4$, 940 (12); **7**: MS (DCI, NH_3) m/z (rel. int.) 1081 (1) $R_3Sb_3Se_3$, 720 (1) $R_2Sb_2Se_2$, R = $(Me_3Si)_2CH$. An X-Ray structure analysis showed, that **5** is an eight membered $(RSbO)_4$ ring in the boat form with the substituents in trans positions[4].The ^{1}H-NMR spectra of 5 - 7 in $CDCl_3$ show three signals for the Me_3Si protons. (**5**: δ = 0,179s [18H]; 0,180 s [18H]; 0,181 s [18H] (CH_3); 0,77 [3H] (CH); **6**: 0,211 s [18H], 0,219 s [18H], 0,230 s [18H], CH_3; 0,74 s [1H], 0,86 s [2H] CH. **6**: 0,22 s [18H], 0,23 s [18H], 0,24 s [18H], CH_3; 0,77 s [1H], 0,97 s [2H], CH). These spectra are not compatible with the exclusive existence of tetramers in solution. A possible rationalization is the assumption of equilibria between tetramers and trimers $(RSbE)_n$ with cis-trans substituents.

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