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Polyhedron 22 (2003) 1719–1723

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Syntheses of isobutylantimony compounds, *cyclo*-R_nSb_n ($n = 4, 5$), R_4Sb_2, and crystal structure of R_3SbBr_2; R = Me_2CHCH_2

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Received 13 March 2003; accepted 5 May 2003

Abstract

Dehalogenation reactions of $RSbBr_2$ or R_2SbBr (R = Me_2CHCH_2) with Mg in tetrahydrofuran give *cyclo*-R_nSb_n (**1**, $n = 4$, 5) or R_4Sb_2 (**2**). R_3SbBr_2 (**3**) is formed by addition of Br_2 to R_3Sb. The crystals of **3** consist of trigonal bipyramidal molecules with apical bromine atoms.

Keywords: Antimony; Bromine; Isobutyl group; Ring–ring equilibrium; X-ray diffraction; NMR spectra

1. Introduction

In the field of organo antimony homocycles, *cyclo*-R_nSb_n ($n = 3$–6) [1] the chemistry of five membered rings, *cyclo*-R_5Sb_5 (pentastiboles) is particularly manifold. Many five membered rings with aryl, *n*-alkyl or isopropyl substituents exist in solution in equilibria with cyclotetramers. Solid phases of these ring systems consist however of hexamers (R = Ph, Tol [2]) or polymers (R = Et, *n*-Pr, *n*-Bu [3], *i*-Pr [4]). Neopentyl- and trimethylsilylmethyl-pentastiboles are the only five membered organo antimony rings which remain intact on crystallisation and recently the first crystal structures of pentastibole derivatives, i.e. *cyclo*-R_5Sb_5 (R = Me_3CCH_2 [5]) and *cyclo*-$R_5Sb_5[W(CO)_5]_2$ (R = Me_3SiCH_2 [6]) were reported. Expecting that also the isobutyl group might be suitable for the stabilisation of pentastiboles we studied *cyclo*-R_nSb_n, (R = Me_2CHCH_2; **1a**, $n = 4$; **1b**, $n = 5$) and included also the corresponding distibine, R_4Sb_2 (**2**) and trialkylantimony dibromide R_3SbBr_2 (**3**) in the investigations. Previously reported isobutyl antimony compounds, i.e. R_3Sb [7], R_2SbX (X = H, Br, I), $RSbX_2$ (X = H, Br) and R_3SbI_2 (R = Me_2CHCH_2) were studied as precursors for chemical vapour deposition processes [8].

2. Experimental

The NMR spectra were recorded on Bruker DPX 200 and AVANCE DRX-600 instruments. Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.15 ppm, ^1H) and C_6D_6 (128.0 ppm, ^{13}C). The C, H correlation was performed with use of the HSQC spectra. Mass spectra were recorded on Finnigan MAT CH7 (A) and Finnigan MAT 8222 spectrometers. The pattern of antimony-containing ions was compared with theoretical values. Elemental analyses were performed by Mikroanalytisches Laboratorium Beller in Göttingen. The syntheses were carried out in argon atmosphere using dried solvents distilled under argon. R_3Sb, $RSbBr_2$ and R_2SbBr (R = Me_2CHCH_2) were prepared according to reported procedures [8].

2.1. Synthesis of *cyclo*-(*i*-Bu_nSb_n) (**1a**, $n = 4$; **1b**, $n = 5$)

A solution of 22.7 g (67.0 mmol) of *i*-$BuSbBr_2$ in 100 ml tetrahydrofuran (thf) was added dropwise with stirring to 1.84 g (76.7 mmol) of magnesium filings activated with 1,2-dibromoethane. The reaction mixture was stirred for 12 h and the solvent was removed in

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00333-4

vacuo. Washing the black remaining product mixture with petroleum ether gave an orange solution, which was reduced to 10 ml, combined with Al_2O_3 (2 g), dried to a flowing powder under reduced pressure and placed on a chromatography column (15 × 2 cm, Al_2O_3, activity level II). With petroleum ether an orange fraction was eluted. Removal of the solvents under reduced pressure gave 4.1 g (34%) of **1** as orange crystals. ^{1}H NMR (C_6D_6, 600 MHz): **1a**, 1.028 (d, $^3J_{HH} = 6.7$ Hz, 24H; CH_3), 2.12–2.19 (m, 4H; CH), 2.293 (d, $^3J_{HH} = 6.9$ Hz, 8H; CH_2); **1b**, 1.0139 (d, $^3J_{HH} = 6.4$ Hz, 24H; CH_3), 1.0368 (d, $^3J_{HH} = 6.7$ Hz, 6H; CH_3), 1.95–2.05 (m, 5H; CH), AB parts of ABX spin systems with A 2.3916, B 2.5005 ($^2J = 11.9$ Hz, $^3J = 6.9$ Hz, 4H; CH_2), A 2.4400, B 2.5623 ($^2J = 11.9$ Hz, $^3J = 6.7$ Hz, 4H; CH_2), 2.3992 (d, $^3J = 6.9$ Hz, 2H; CH_2). ^{13}C NMR (C_6D_6, 50 MHz): **1a**, 23.72 (CH_2), 25.92 (CH_3), 30.39 (CH); **1b**, 20.92, 21.30, 23.18 (CH_2), 25.32, 25.41, 25.45, 25.47 (CH_3), 31.24, 31.40, 31.53 (CH). MS (EI, 70 eV): m/z (%) 894 (2) [$R_5Sb_5^+$], 837 (7) [$R_4Sb_5^+$], 716 (2) [$R_4Sb_4^+$], 659 (5) [$R_3Sb_4^+$], 536 (9) [$R_3Sb_3^+$], 479 (2) [$R_2Sb_3^+$], 423 (8) [RSb_3^+], 367 (18) [Sb_3^+], 179 (7) [RSb^+], 57 (100) [R^+] ($R = C_4H_9$).

2.2. Synthesis of *i*-Bu$_4$Sb$_2$ (**2**)

6.3 g (19.9 mmol) *i*-Bu$_2$SbBr in 50 ml thf was added dropwise with stirring to 0.53 g (22.08 mmol) of magnesium filings activated with 1,2-dibromoethane. The mixture was stirred for 12 h and the solvent was removed in vacuo. Washing the black residue with petroleum ether, gave a yellow solution. Removal of the solvent at 50 mbar and distillation at 5×10^{-2} mbar, bp 35–40 °C yielded 4.6 g (48.8%) **2** as a yellow oil. *Anal*. Calc. For $C_{16}H_{36}Sb_2$: C, 40.71; H, 7.68%. Found: C, 40.43; H, 7.78. ^{1}H NMR (C_6D_6, 600 MHz): 1.019 (d, $^3J = 6.6$ Hz, 24H; CH_3), AB part of an ABX spin system with A 1.68, B 1.97 ($^2J_{HH} = 11.9$ Hz, $^3J_{HH} = 6.9$ Hz, 8H; CH_2), 1.90 (h, $^3J_{HH} = 6.6$ Hz, 4H; CH). ^{13}C NMR (C_6D_6, 50 MHz): 22.79 (CH_2), 25.78 (CH_3), 29.39 (CH). MS (EI, 70 eV): m/z (%) 472 (100) [M^+], 416 (20) [M^+-R], 359 (30) [M^+-2R], 301 (20) [M^+-3R], 179 (20) [RSb^+], 57 (10) [R^+] ($R = C_4H_9$).

2.3. Synthesis of *i*-Bu$_3$SbBr$_2$ (**3**)

A solution of Br_2 (0.7 g, 4.37 mmol) in petroleum ether (20 ml) was added to *i*-Bu$_3$Sb (1.32 g, 4.5 mmol) in 30 ml petroleum ether at −20 °C. After the addition, the mixture was warmed up to room temperature. Slow evaporation of the solvent gave 1.6 g (78.4%) of **3** as colorless crystals, m.p. 90 °C, (Ref. [9], m.p. 88–95 °C). *Anal*. Calc. for $C_{12}H_{27}Br_2Sb$: C, 31.82; H, 6.01%. Found: C, 31.69; H, 6.08. ^{1}H NMR (C_6D_6, 200 MHz): 0.88 (d, $^3J_{HH} = 6.6$ Hz, 18H; CH_3), 2.52 (h, $^3J_{HH} = 6.8$ Hz, 3H; CH), 2.77 (d, $^3J_{HH} = 6.9$ Hz, 6H; CH_2). MS (EI, 70 eV): m/z (%) 395 (14) [M^+-R], 373 (84) [M^+-Br], 316 (14) [R_2SbBr^+], 259 (5) [$RSbBr^+$], 179 (44) [RSb^+], 57 (100) [R^+] ($R = C_4H_9$).

2.4. X-ray crystallography of *i*-Bu$_3$SbBr$_2$ (**3**)

Formula $C_{12}H_{27}Br_2Sb$, M = 452.91, colorless crystals 0.7 × 0.6 × 0.5 mm, rhombohedral space group R-3, radiation Mo Kα $\lambda = 0.71073$ Å, $a = 9.8176(10)$, $b = 9.8176(10)$ Å, $c = 30.712(6)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 2563.55$ Å^3, $Z = 6$, $\rho_{calc} = 1.760$ Mg m^{-3}, absorption coefficient 6.267 mm^{-1}, $F(0\,0\,0)$ 1320, $T = 173$ K, θ range for data collection 2.74°–27.50°, index range $-11 \leq h \leq 11$, $-12 \leq k \leq 11$, $-39 \leq l \leq 39$, 7686 reflections collected, 1313 independent reflections, $R(\text{int}) = 0.0438$, Siemens P4 four cycle diffractometer, completeness to $\theta = 27.50°$ 99.5%, DIFABS absorption correction, refinement method Full-matrix least-squares on F^2, data/restraints/parameter 1313/0/52, goodness-of-fit on F^2 1.099, final R-indices [$I > 2\sigma(I)$] $R_1 = 0.0245$ $wR_2 = 0.0551$, (all data) $R_1 = 0.0361$ $wR_2 = 0.0594$, largest difference peak and hole 0.893 and −0.305 e Å^{-3}. The positions of the hydrogen atoms were calculated with a riding model.

3. Results and discussion

Isobutylantimony rings, R_nSb_n (**1**, $R = Me_2CHCH_2$) were obtained as yellow air sensitive crystals well soluble in hydrocarbons by dehalogenation of isobutylantimony dibromide with magnesium in thf. The yield of the ring products **1** is 34%. The residual product is a black insoluble solid, containing probably a polymeric form of isobutylantimony. Solutions of the rings in C_6D_6 (c(**1**) = 3.06×10^{-3} mol l^{-1}) contain 4 mol.% of the tetramer *cyclo*-R_4Sb_4 (**1a**) and 96 mol.% of the pentamer *cyclo*-R_5Sb_5 (**1b**) (Eq. (1)).

$$RSbBr_2 + Mg \rightarrow 1/n \ cyclo\text{-}R_nSb_n + MgBr_2$$

$$R = Me_2CHCH_2 \quad \mathbf{1a},\ n = 4; \quad \mathbf{1b},\ n = 5 \qquad (1)$$

The identity of **1a** and **1b** was proven by the observation of the molecular ions in the mass spectra and by NMR spectroscopic investigations in solution. The ^{1}H NMR spectra of **1a** and **1b** in C_6D_6 at room temperature obtained at 600 MHz are depicted in Fig. 1(c). The intense signals result from the five membered ring **1b**, where the isobutyl groups adopt a maximum of *trans* positions. Particularly characteristic are the patterns for the protons of the methylene group. There are eight doublet signals corresponding to the AB parts of two ABX spin systems for the diastereotopic CH_2 groups at the two pairs of chiral centers Sb_2, Sb_5 and Sb_3, Sb_4, one doublet for the CH_2 groups at Sb_1 as well as a complex multiplet and overlapping signals for the

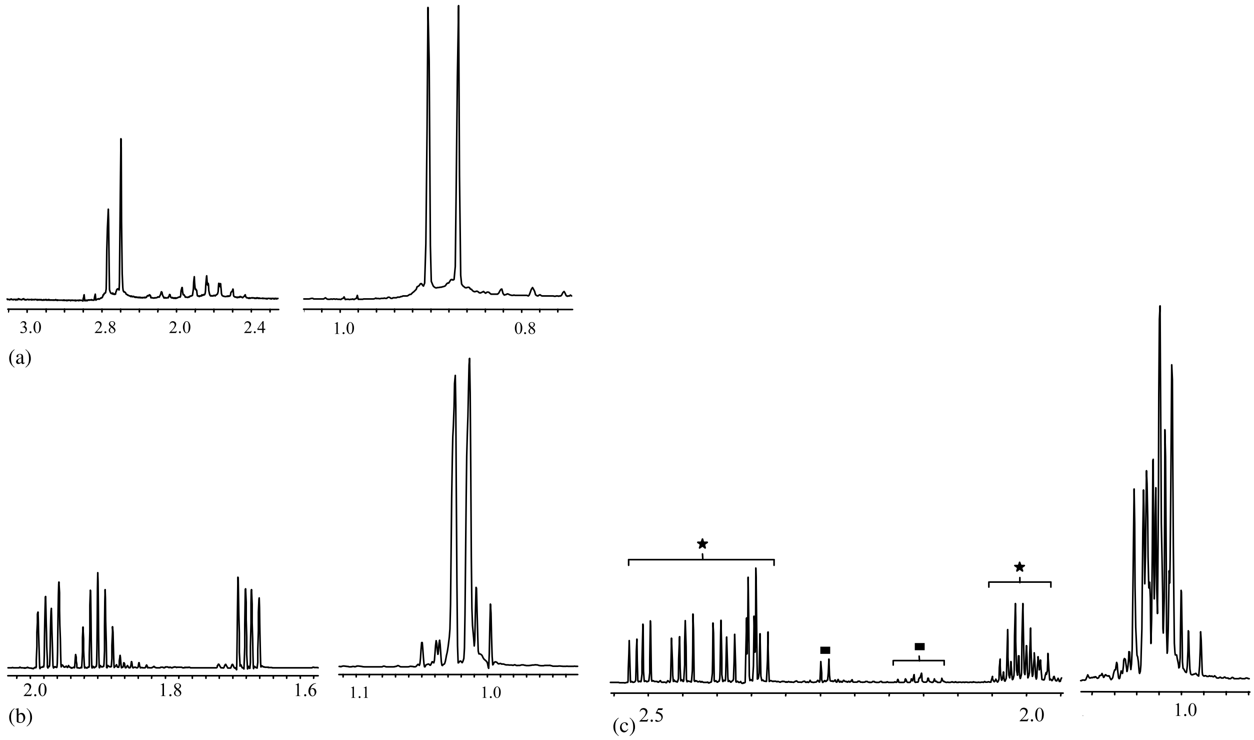
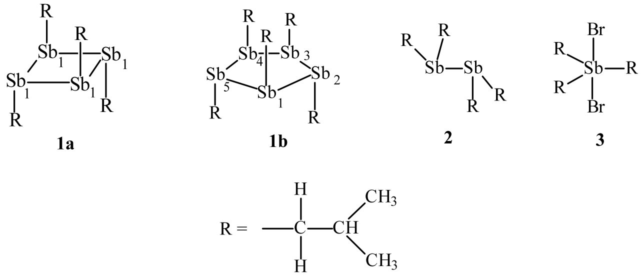


Fig. 1. Part of the ^{1}H NMR spectra of: (a) $(Me_2CHCH_2)_3SbBr_2$ (**3**) (200 MHz); (b) $(Me_2CHCH_2)_4Sb_2$ (**2**) (600 MHz); (c) $(Me_2CHCH_2Sb)_n$ ((■) $n = 4$, **1a**; (★) $n = 5$, **1b**) (600 MHz). The chemical shifts are given in δ values.

CH and CH_3 groups. The signals of the four membered ring **1a** where all the isobutyl groups are equivalent have only low intensities. The fraction of **1a** increases however on the cost of **1b** on dilution due to the equilibrium between the rings. The value for $K = [\mathbf{1b}]^4/[\mathbf{1a}]^5$ is 2.06×10^8 mol l^{-1}. Characteristic signals for **1a** and **1b** are also observed in the ^{13}C NMR spectra. For **1b** there are four CH_3 signals with an approximate 1:1:2:1 ratio of intensities instead of the five signals of equal intensity which are expected due to diastereotopic effects. Mass spectra contain molecular ions and characteristic fragments not only of **1a** and **1b** but with relative high intensities also for the trimer R_3Sb_3. The most intense antimony signals correspond to Sb_3^+. The cyclic form of this interesting ion is an aromatic 2π system analogous to a cyclopropenium ion.

The rings **1a** and **1b** decompose with formation of tetraisobutyldistibane (**2**). Even freshly prepared samples contain **2** as an impurity and therefore elemental analyses did not give meaningful results. Attempts to characterise the yellow solid by an X-ray structure analysis failed because suitable single crystals were not obtained (scheme 1).

Tetraisobutyldistibane R_4Sb_2 (**2**) is also formed by reduction of *i*-Bu_2SbBr with Mg in thf (Eq. (2)). After purification a yield of 49% is obtained. **2** is an yellow air sensitive oil, which is soluble in organic solvents and thermally stable in an inert atmosphere.



Scheme 1.

$$2R_2SbBr + Mg \rightarrow R_4Sb_2 + MgBr_2$$

$$R = Me_2CHCH_2 \qquad (2)$$

The characterisation of **2** is achieved by elemental analysis, NMR and mass spectrometry. The ^{1}H NMR spectrum measured at 600 MHz is shown in Fig. 1(b). It contains a multiplet for the methyl protons and eight signals of the AB part of an ABX spin system for the CH_2 group. The signal for the CH protons consists of seven lines of a multiplet resulting from coupling with the neighbouring groups. The spectrum clearly reflects the diastereotopic character of the methylene protons. Three lines for the different carbon atoms of the isobutyl group appear in the ^{13}C NMR spectrum. The mass spectrum shows the molecular ion and characteristic fragments of **2**.

Triisobutylantimony dibromide (**3**) is prepared in 78% yield by addition of bromine to *i*-Bu_3Sb analogous to procedures described in the earlier literature [9]. The dibromide is a colourless air stable crystalline compound, soluble in hydrocarbons. The ^1H NMR spectrum in C_6D_6 reveals the presence of equivalent alkyl groups corresponding to the trigonal bipyramidal arrangement with axial bromine atoms. The mass spectrum contains fragment ions resulting from removal of *i*-Bu groups and Br atoms at highest mass. The composition is confirmed by the elemental analysis. An X-ray structure determination was carried out on single crystals obtained from petroleum ether. The molecular structure is depicted in Fig. 2.

The coordination at antimony is trigonal bipyramidal with only small deviations from the ideal values for this geometry. The antimony atom is situated 0.0876 Å above the plane formed by the C(1) atoms of the *i*-Bu substituents. The Sb–Br bond lengths in **3** (Sb(1)–Br(1) 2.6654(7) Å, Sb(1)–Br(2) 2.6289(7) Å) compare well with the corresponding values in other trialkylantimony dibromides, R_3SbBr_2 (R = Me, 2.649 Å [10]; R = $(Me_3Si)_2CH$, 2.672(1), 2.657(1) Å [11]; R = $C_6H_5CH_2$, 2.669(1), 2.623(1) Å [12]). The Me_2CH groups are all orientated in the same sense, in a propeller like manner (H–C–C–Sb 47.54(1)°), avoiding close contacts between each other. C(3) lies −0.3616 Å below and C(4) 1.3345 Å above the Sb(1), C(1) and C(2) plane with dihedral angles Sb(1)–C(1)–C(2)–C(3) = 165.45(1)° and Sb(1)–C(1)–C(2)–C(4) = −71.72(1)°. Between the molecules of **3** there are no close intermolecular contacts. The shortest intermolecular Br–Br and Sb–Br distances are > 5 Å and > 6 Å. Shorter intermolecular Br–Br distances exist in R_3SbBr_2 (R = $(Me_3Si)_2CH$, 3.473(1) Å [11]; R = Me, 3.59 Å [10]; R = $C_6H_5CH_2$, 4.17 Å [12].

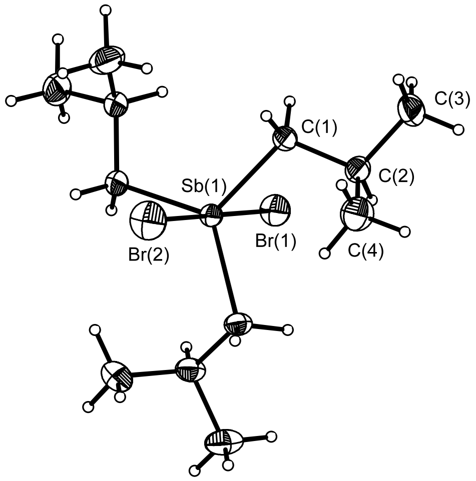


Fig. 2. ORTEP-like representation at 50% probability of $(Me_2CHCH_2)_3SbBr_2$ (**3**) showing the atomic numbering scheme. Selected distances (Å) and angles (°): Sb(1)–C(1) 2.130(2), Sb(1)–Br(1) 2.6654(7), Sb(1)–Br(2) 2.6289(7), C(1)–Sb(1)–C(1)* 119.832(9), C(1)–Sb(1)–Br(1) 87.64(6), C(1)–Sb(1)–Br(2) 92.36(6), Br(1)–Sb(1)–Br(2) 180.0, C(2)–C(1)–Sb(1) 112.82(15); H(2)–C(2)–C(1)–Sb(1) 47.54(1), Sb(1)–C(1)–C(2)–C(3) 165.45(1), Sb(1)–C(1)–C(2)–C(4) −71.72(1).

4. Conclusion

The isobutylantimony ring systems is closely related to the analogous neopentyl and trimethylsilyl rings where cyclopentamers with substituents adopting a maximum of *trans* positions are dominating in solution and in the solid state. Ring–ring equilibria in solutions lead only to small fractions of tetramers. For spectroscopic and preparative studies now well characterised alkyl antimony five membered rings are available, which are useful as sources for the syntheses of complexes with a wide variety of $(RSb)_n$ or Sb_n ligands. The isobutyl antimony rings system **1** and tetraisobutyldistibane **2** contain substituents capable for beta elimination processes and therefore they are of interest also as antimony components of MOCVD processes. With triisobutylantimony dibromide (**3**) now three crystal structures of trialkylantimony dibromide are known. They all posses covalent trigonal bipyramidal structures with axial bromine atoms.

5. Supplementary material

Supplementary crystallographic data of compound **3** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 205000. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Britta Röskam and Andreas Suchopar for experimental help and the Deutsche Forschungsgemeinschaft and the University of Bremen for financial support.

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