Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 677 (2003) 15–20
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Syntheses and coordination chemistry of di-, tri-, and tetrastibanes, $R_2Sb(SbR')_nSbR_2$ ($n = 0, 1, 2$)

Hans Joachim Breunig *, Ioan Ghesner, Mihaiela Emilia Ghesner, Enno Lork

Institut für Anorganische und Physikalische Chemie, Universität Bremen, Fachbereich 2, Postfach 330 440, D-28334 Bremen, Germany

Received 24 January 2003; received in revised form 11 March 2003; accepted 20 March 2003

Abstract

Syntheses of the stibanes, $^tBu_2Sb(SbMe)_nSb^tBu_2$ [$n = 1$ (**1**), 2 (**2**)], ($^tBu_2Sb)_2$ (**3**), $Mes_2Sb(SbPh)_nSbMes_2$ [$n = 1$ (**4**), 2 (**5**)] and of complexes with stibane ligands, $[(CO)_5Cr]_2(Me_2Sb)_2$ (**6**), $[Cr(CO)_4(Me_2Sb(SbR)_2SbMe_2)]$ (**7**), $[Cr(CO)_4(Ph_2Sb–SbPh–SbR–SbPh_2)]$ (**8**) ($R = CH_2SiMe_3$) are reported. The crystal structures of **6** and **8** were determined by X-ray diffraction.

Keywords: Antimony; Chromium complexes; X-ray structure analyses

1. Introduction

Organometallic compounds with antimony–antimony single bonds are well known as distibanes, $(R_2Sb)_2$ and cyclostibanes, $(RSb)_n$ ($n = 3–6$) [1]. Much less developed is the chemistry of *catena*-stibanes, $R_{(n+2)}Sb_n$ that are of interest as one-dimensional substances [2]. Previously known examples [3,4] of *catena*-stibanes are ill-defined polymers or components of ring-chain equilibria (Eq. (1)).

$$cyclo\text{-}(SbR')_n + R_2Sb–SbR_2 \rightleftharpoons catena\text{-}R_2Sb–(SbR')_n–SbR_2 \quad (1)$$

Recently we were able to trap and to fully characterize the first tetrastibanes as ligands in chromium carbonyl complexes [4]. The phosphorus analogues of *catena*-stibanes have received more attention and several well defined examples [5,6] and also complexes with *catena*-phosphane or -arsane ligands [7,8] were reported. Famous extended one-dimensional systems are the ladder structure of methyl arsenic [9] and the linear chains of tetramethyldistibane [10]. We report here on the protection of *catena*-tri- and tetrastibanes by bulky organic groups (^{t}Bu, Mes, Me_3SiCH_2) and on the formation and structures of complexes with di- and tetrastibane ligands.

2. Results and discussion

2.1. Syntheses of sterically protected stibanes

Tri- and tetrastibanes bearing terminal *tert*-butyl groups form by reduction of $^tBu_2SbCl$ and $MeSbCl_2$ (2:1 molar ratio) with magnesium in tetrahydrofuran (Eq. (2)). The novel *catena*-stibanes, $^tBu_2Sb(SbMe)_nSb^tBu_2$ [$n = 1$ (**1**), 2 (**2**)] are obtained as an yellow air sensitive liquid which is readily soluble in organic solvents. The tristibane **1** which corresponds to the stoichiometry of the reagents is formed in 30% yield. The unexpected formation of **2** (13%) is probably related to the sterically less congested situation in this tetrastibane. The remaining products of the reduction are brown solids which are insoluble in hydrocarbons. They probably contain highly polymeric congeners of **1** and **2**.

$$R_2SbCl \xrightarrow[-MgCl_2]{+MeSbCl_2+Mg/THF,\ 25\ ^\circ C} R_2Sb(SbMe)_nSbR_2 \quad (2)$$

where $R = {}^t$Bu; **1**: $n = 1$; **2**: $n = 2$.

Attempts to separate **1** and **2** by column chromatography or other methods led to decomposition. The novel *catena*-stibanes were identified by their ^{1}H-NMR spectra in C_6D_6 (Fig. 1a). For each stibane there are

* Corresponding author. Tel.: +49-421-218-2266; fax: +49-421-218-4042.
E-mail address: breunig@chemie.uni-bremen.de (H.J. Breunig).

0022-328X/03/$ - see front matter
doi:10.1016/S0022-328X(03)00320-6

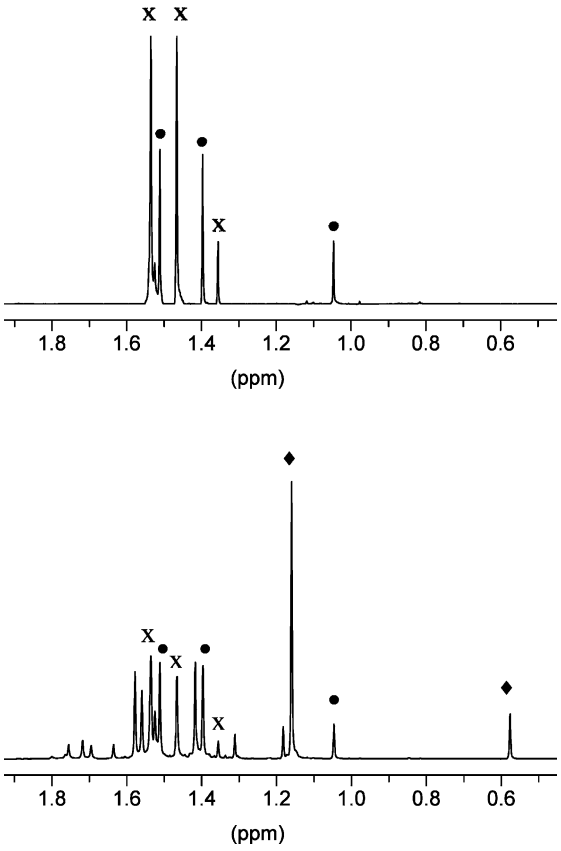


Fig. 1. ^{1}H-NMR spectra of **1** (×) and **2** (●) in C_6D_6; above: a fresh sample; below: sample after 1 day at room temperature with formation of ^{t}Bu$_2$SbMe (◆) and other products.

three characteristic signals, a pair of singlet signals of equal intensity for the diastereotopic ^{t}Bu groups and singlet signals for the methyl groups.

Separate signals for the *meso*- and *d*, *l* form of the tetrastibane **2** were not observed. Most likely only one of the isomers is present in solution. In an alternative explanation the inversion of configuration at the central antimony atoms might be assumed. This process is however unlikely to be fast at the NMR time scale. **1** and **2** are the first *catena*-stibanes which exist in solution in the absence of di- and *cyclo*-stibanes. The sterical influence of the ^{t}Bu groups is sufficient to protect the terminal Sb–Sb bonds and also to disfavour the formation of (^{t}Bu$_2$Sb)$_2$ (**3**) during the syntheses. Despite the sterical protection **1** and **2** are not stable at room temperature for a long time. They decompose in the course of hours with migration of methyl groups and formation of ^{t}Bu$_2$SbMe and other products. This decomposition can be followed in the ^{1}H-NMR spectra where the two singlets assigned to ^{t}Bu$_2$SbMe become the most intense signals after 1 day. The spectra (Fig. 1) show that the sterically more congested tristibane **1** decomposes faster than **2**. The varying **1**:**2** ratio during the decomposition confirms unambiguously the assignment of the ^{1}H-NMR signals. The high reactivity of the novel *catena*-stibanes is also reflected in the mass spectra, which show signals for fragment ions of **1** and for various decomposition products.

In other approaches for the syntheses of *catena*-stibanes with terminal ^{t}Bu$_2$Sb groups we also investigated the reactions of [(^{t}Bu$_2$Sb)$_2$Sb][K(pmdeta)] (pmdeta = pentamethyldiethylenetriamine) [11] with MeI or Me_3SiCH_2Cl in THF or toluene between −80 and −30 °C. We were able to prove the formation of **1** and a rearrangement product, ^{t}Bu$_3$Sb$_2$CH$_2$SiMe$_3$ by NMR methods, and mass spectrometry but found that the reactions were not useful for synthetic purposes. Also reactions of cyclostibanes, (RSb)$_n$ (R = ^{t}Bu, R = CH_2SiMe_3, $n = 4$, 5) with (^{t}Bu$_2$Sb)$_2$ (**3**) were investigated in NMR tube experiments in C_6D_6. At room temperature no reaction occurred even with excess of **3**. Heating the solutions leads to decomposition of the distibane reagent. The synthesis of **3** was achieved in 83% yield and high purity in a new way simply by adding ^{t}Bu$_2$SbCl to $LiAlH_4$. The reverse procedure (i.e. addition of $LiAlH_4$ to ^{t}Bu$_2$SbCl) gives ^{t}Bu$_2$SbH [12]. Previously reported methods for the preparation of **3** [12,13] are more complicated and we found it difficult to obtain a pure product.

Catena-tri- and tetra-stibanes exist also with mesityl substituents in terminal positions. Reaction of Mes_2SbLi with $PhSbCl_2$ at −70 °C in a 2:1 stoichiometry (Eq. (3)) gives **4** in 16% together with **5** in 4% yield. The remaining products are insoluble materials, probably polymeric arylstibanes.

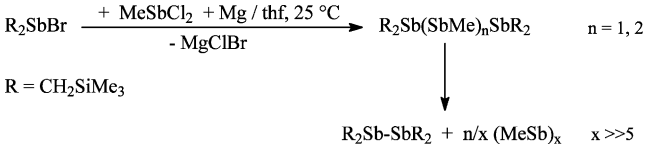
$$Mes_2SbLi \xrightarrow[-LiCl]{+PhSbCl_2/THF,\ -70\ ^\circ C} Mes_2Sb(SbPh)_nSbMes_2 \quad (3)$$

where **4**: $n = 1$; **5**: $n = 2$

Compounds **4** and **5** are air sensitive, but stable in an inert atmosphere at room temperature for several days. The ^{1}H-NMR spectra show the characteristic pattern for the diastereotopic mesityl groups of the peripheral Mes_2Sb unit, i.e. three sets of two singlets for the *ortho* methyl protons, *para* methyl protons and for the *meta* protons for each compound. In the EI mass spectra the decomposition product Mes_2PhSb^+ was identified.

Also the dehalogenation of a mixture of (Me_3SiCH_2)$_2$SbBr and $MeSbCl_2$ with magnesium at room temperature leads orange soluble products and black solids. The former probably consist of tri- and tetrastibanes, *catena*-R$_2$Sb(SbMe)$_n$SbR$_2$ ($n = 1$, 2; R = CH_2SiMe_3), the latter of polymeric stibanes. However, the sterical protection of the oligo stibanes by terminal trimethylsilylmethyl groups is not sufficient and decomposition occurs already during the work-up procedures with formation of R$_2$Sb–SbR$_2$ (R = CH_2SiMe_3) [14] and a black polymeric form of methylantimony, (MeSb)$_x$

[15]. In Eq. (4) features a new synthetic path for this interesting material.



(4)

2.2. Complexes with stibane ligands

For the study of the role of the organic groups in the chemistry of *catena*-stibanes it is useful to compare compounds with reverse positions of the organic substituents. Tri- and tetrastibanes with terminal methyl- and central trimethylsilylmethyl-groups, i.e. $Me_2Sb(SbR)_nSbMe_2$ ($n = 3$, 4; $R = CH_2SiMe_3$) were found only in equilibria with $Me_2Sb–SbMe_2$ and *cyclo*-$(RSb)_n$ ($n = 4$, 5). After successfully trapping the tetrastibane from the equilibrium mixture we tried to isolate also the tristibane by complexation and reacted the equilibrium mixture with $[THFCr(CO)_5]$ in THF. However instead of the formation of a tristibane complex, the coordination of the distibane and the tetrastibane occurred and $[(CO)_5Cr]_2(Me_2Sb)_2$ (**6**) [16] and *cyclo*-$[Cr(CO)_4Me_2Sb(SbR)_2SbMe_2]$ ($R = CH_2SiMe_3$) (**7**) [4] were obtained in 60 and 8% yield. The structure of the distibane complex was determined by an X-ray diffraction study on single crystals of **6**·C_6H_6. The molecular structure is depicted in Fig. 2. **6** is the first transition metal complex of tetramethyldistibane studied by X-ray crystallography. The coordination of the distibane leads to wider angles and shorter bonds at the antimony atoms (Me_4Sb_2/**6**: SbC_2 92.2–95.2°/99.2(18)–100.34(16)°, CSbSb 94.27–94.65°/96.41(11)–102.44(11)°; Sb–Sb 2.84/2.8097(9) Å). These changes of the geometry probably result from an increase of s-orbital participation from the p^3 configuration of the antimony atoms in Me_4Sb_2 to closer to sp^3 in **6**. The Sb–Cr (2.625 Å) distances in **6** compare well with those found in **7** (Sb–Cr 2.6087 Å [4]). An unusual feature of **6** is a substantial deviation (dihedral angle lp-Sb–Sb-lp = 160°, lp = lone pair of electrons at Sb) from the ideal antiperiplanaric (*trans*) conformation (lp-Sb–Sb-lp = 180°) which was found in solid Me_4Sb_2 [10] and $[(CO)_5M]_2(Ph_2Sb)_2$ (M = Cr [17], W [18]) Table 1.

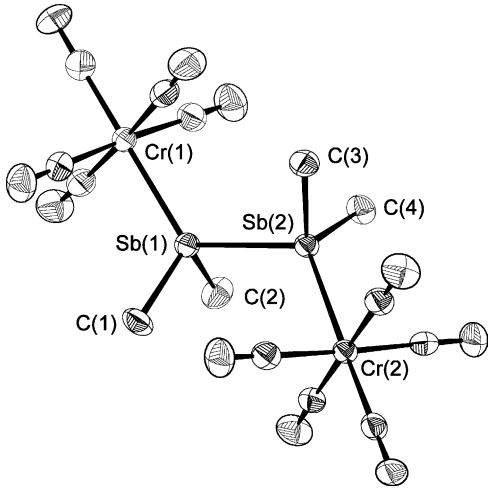


Fig. 2. ORTEP-like representation at 50% probability of **6** showing the atomic numbering scheme. Selected distances (Å) and angles (°): Sb(1)–Sb(2) 2.8097(9), Sb(1)–C(1) 2.132(4), Sb(1)–C(2) 2.150(4), Sb(2)–C(3) 2.141(3), Sb(2)–C(4) 2.135(3), Sb(1)–Cr(1) 2.629(9), Sb(2)–Cr(2) 2.621(8), C(1)–Sb(1)–C(2) 99.20(18), C(3)–Sb(2)–C(4) 100.34(16), Cr(1)–Sb(1)–Sb(2) 122.39(3), Cr(2)–Sb(2)–Sb(1) 118.33(2).

The formation of **7** is remarkable because the tetrastibane is only a minor component in the initial stibane mixture and also because $Cr(CO)_4$ units do not form easily from $[THFCr(CO)_5]$ at low temperatures. In fact

Table 1
Crystallographic data and measurements for **6**·C_6H_6 and **8**

Compound	**6**·C_6H_6	**8**
Empirical formula	$C_{14}H_{12}Cr_2O_{10}Sb·C_6H_6$	$C_{38}CrH_{36}O_4Sb_4Si$
Formula weight	765.84	1123.76
Colour	Yellow	Orange
Crystal size, (mm)	0.5 × 0.35 × 0.3	0.5 × 0.4 × 0.3
Unit cell dimensions		
a (Å)	15.233(3)	11.27(2)
b (Å)	11.556(2)	12.549(3)
c (Å)	16.73(3)	15.296(3)
α (°)	90	83.94(3)
β (°)	107.15(3)	72.60(3)
γ (°)	90	81.63(3)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
Z	4	2
Diffractometer	stoe IPDS	stoe IPDS
Mo–K_α (Å)	0.71073	0.71073
Temperature (K)	173(2)	173(2)
Reflections collected	39 116	29 045
Independent reflections	5486	7379
R_{int}	0.0455	0.0525
Completeness to θ (%)	98.2	92.9
Absorptions coefficient (mm^{-1})	2.696	2.940
Absorption correction	DIFABS	DIFABS
Final R^a indices	$R_1 = 0.0254$	$R_1 = 0.0216$
$[I > 2\sigma(I)]$	$wR_2 = 0.0669$	$wR_2 = 0.0431$
R^a indices (all data)	$R_1 = 0.0325$, $wR_2 = 0.069$	$R_1 = 0.0343$, $wR_2 = 0.0450$
Goodness-of-fit on F^2	1.010	0.883
Data/restraints/parameters	5486/0/343	7379/0/452
Largest difference peak and hole (e $Å^{-3}$)	1.051, −0.66	0.636, −0.498

[a] Definition of the R values: $R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; $wR_2 = \{[w\Sigma(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_0^2)+(\alpha P)^2+bP$.

[nbdCr(CO)$_4$] (nbd = norbornadiene) is much more efficient for trapping the tetrastibanes.

In a re-examination of the synthesis of *cyclo*-[Cr(CO)$_4$(Ph$_2$Sb–SbR–SbR–SbPh$_2$)] (R = CH$_2$SiMe$_3$) from *cyclo*-(Me$_3$SiCH$_2$Sb)$_n$ ($n = 4$, 5), (Ph$_2$Sb)$_2$ and [nbdCr(CO)$_4$] [4] we have isolated *cyclo*-[Cr(CO)$_4$-(Ph$_2$Sb–SbPh–SbR–SbPh$_2$)] (R = CH$_2$SiMe$_3$) (**8**), an interesting side product formed by migration of substituents. This novel complex contains the first tetrastibane ligand with two different chiral antimony centers and where four optical isomers are possible. An X-ray diffraction study revealed that only two isomers, the enantiomers of the *threo* form are present in crystals of **8**. The structure (Fig. 3) features a five membered chelate ring where the Sb(2)–Sb(3) unit is twisted by 23° out of the Sb(1)–Cr–Sb(4) plane.

The Sb–Cr bond lengths in **8** (2.6109(11), 2.6065(11) Å) lie in the usual range (Sb–Cr 2.596(8), 2.588(8) Å in **7** [4]). The angles around the antimony atoms (Sb(1) 96.94(13)–116.66(1); Sb(4) 95.86(1)–116.49(1); Sb(2) 93.70(1)–95.82(1); Sb(3) 91.94(1)–97.22(4)°) and the Sb–C bond lengths (four-coordinate Sb–C 2.14(3)–2.15(3) Å and three-coordinate Sb–C 2.175(3)–2.183(3) Å) correspond to sp^3 hybridization and p^3 configurations, respectively, for the four- and three-coordinate antimony atoms. The average Sb–Sb bond distance of 2.8409 Å is consistent with normal single bonds. A remarkable feature of the crystal structure of **8** is the pair wise association of two enantiomers through a short intermolecular contact (3.636 Å) between the Sb(2) atoms which bear parallel phenyl groups. Close intermolecular Sb···Sb contacts were observed repeatedly in crystal structures of distibanes, cyclostibanes, or complexes with *cyclo*-Sb$_3$ ligands [19]. They usually lead to extended arrays. Dimeric association is a new phenomenon which is favored in the case of **8** because with exception of Sb(2) all the antimony atoms are sterically shielded.

The present results mark two important steps in the development of *catena*-stibane chemistry: (i) the first antimony compound with two different Sb chiral centers was isolated and (ii) tri- and tetrastibanes which are not components of ring chain equilibria (Eq. (1)) were synthesized and characterized in solution. However for further progress the thermal stability of the *catena*-

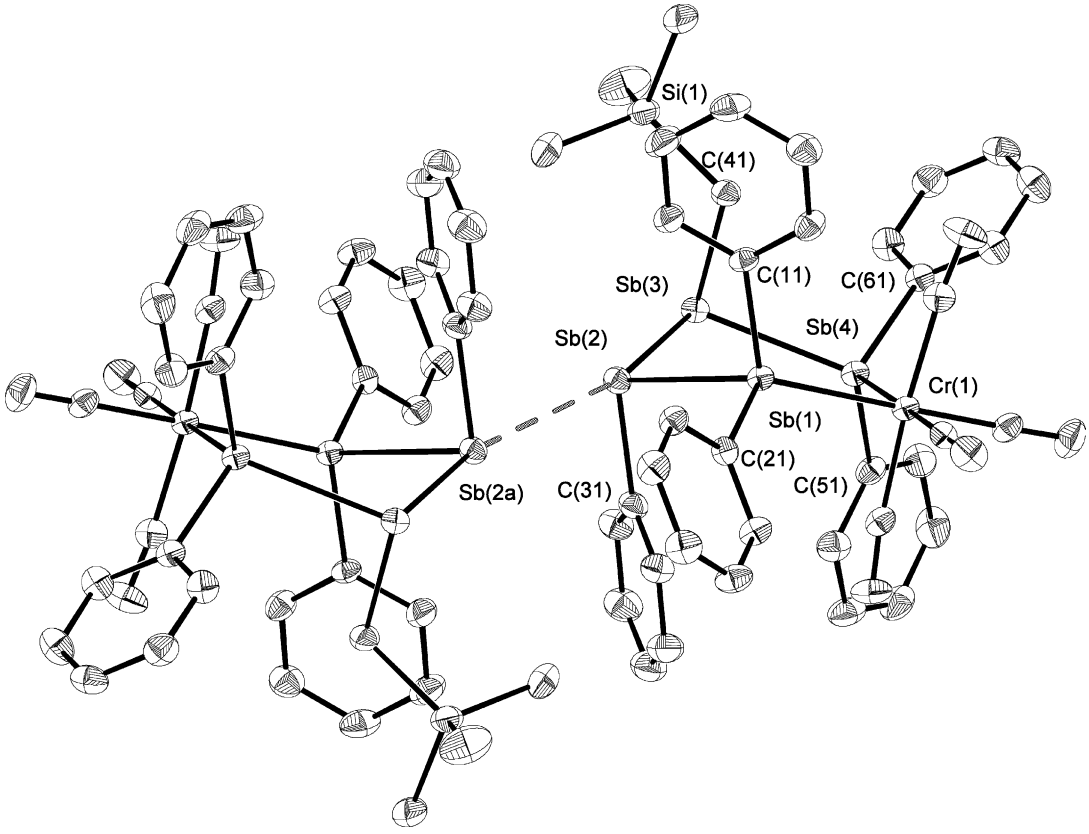


Fig. 3. ORTEP-like representation at 50% probability of (*S*,*S*)-**8** and (*R*,*R*)-**8**, showing the dimeric association and atom numbering scheme for (*S*,*S*)-**8**. Selected distances (Å) and angles (°): Sb(1)–Sb(2) 2.8609(1), Sb(2)–Sb(3) 2.8207(11), Sb(3)–Sb(4) 2.8411(8), Sb(1)–C 2.149(3)–2.150(3), Sb(4)–C 2.140(3)–2.144(4), Sb(2)–C(31) 2.175(3), Sb(3)–C(41) 2.183(3), Sb–Cr 2.6065(11)–2.6109(11), Sb(2)···Sb(2a) 3.636, Sb(1)–Cr(1)–Sb(4) 91.62(3), C(31)–Sb(2)–Sb(3) 93.7(1), Sb(2)–Sb(1)–Cr(1) 120.79(3), C(41)–Sb(3)–Sb(2) 95.92(11), Sb(3)–Sb(4)–Cr(1) 121.89(3), C(41)–Sb(3)–Sb(4) 91.94(1), Sb(1)–Sb(2)–Sb(3) 95.16(3), C–Sb(4)–Sb(3) 95.86(1)–105.3(1), C–Sb(1)–Sb(2) 99.08(9)–103.31(1), C(11)–Sb(1)–C(21) 96.94(13), Sb(2)–Sb(3)–Sb(4) 97.22(4), C(51)–Sb(4)–C(61) 98.88(14), C(31)–Sb(2)–Sb(1) 95.82(1).

stibanes should be increased by choosing less mobile substituents.

3. Experimental

NMR spectra were run on a Bruker DPX 200 spectrometer. 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). 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. The reactions and manipulations were performed in an inert atmosphere of dry argon. $(Me_3SiCH_2)_2SbBr$ [20], $MeSbCl_2$ [21], $PhSbCl_2$ [22] and Mes_2SbLi [23] were prepared according to reported procedures.

3.1. *catena*-$^tBu_2Sb(SbMe)_nSb^tBu_2$ (**1**: $n=1$, **2**: $n=2$)

4.93 g (18.15 mmol) $^tBu_2SbCl$ in 25 ml THF and 1.89 g (9.08 mmol) $MeSbCl_2$ in 15 ml THF were added simultaneously making use of two dropping funnels to 0.5 g (20.83 mmol) Mg filings and the mixture was stirred for 5 h at room temperature (r.t.). Removal of the solvent in vacuo and extraction of the brown residue with 4×120 ml petroleum ether gave an orange solution. Evaporation of the solvent gave 2.56 g of an orange oil containing 30% of **1** and 13% of **2**. ^1H-NMR (C_6D_6, 200 MHz), **1**: 1.05 (s, 3H, $SbCH_3$), 1.46 (s, 18 H, CCH_3), 1.53 (s, 18 H, CCH_3). **2**: 1.35 (s, 6H, $SbCH_3$), 1.42 (s, 18 H, CCH_3), 1.51 (s, 18 H, CCH_3). MS (EI, 70 eV, 100 °C): 550 (4) [$^tBu_3MeSb_3^+$], 472 (1) [$^tBu_4Sb_2^+$], 430 (7) [$^tBu_3MeSb_2^+$], 388 (1) [$^tBu_2Me_2Sb_2^+$], 374 (3) [$^tBu_2MeSb_2^+$], 259 (6) [$MeSb_2^+$], 194 (2) [$^tBuMeSb^+$], 179 (2) [$^tBuSb^+$], 151 (2) [Me_2Sb^+], 57 (100) [$^tBu^+$].

3.2. $^tBu_2Sb-Sb^tBu_2$ (**3**)

A solution of 3.6 g (13.26 mmol) of $^tBu_2SbCl$ in Et_2O (70 ml) was added dropwise to a cold (−80 °C) suspension of $LiAlH_4$ (0.55 g, 14.47 mmol) in Et_2O (30 ml). The mixture was warmed to −50 °C, stirred for 2 h at this temperature and 1 h at −30 °C. The solution was then filtered through a cooled (−30 °C) frit covered with kieselguhr. Removal of the solvent under reduced pressure (20 mbar) gave 2.6 g (83%) of **3** as a yellow solid, decomposing above 7 °C. Attempts were made to grow single crystals from THF or Et_2O solutions but only amorphous solids were obtained. ^1H-NMR (C_6D_6, 200 MHz): 1.36 (s, 36 H, CH_3). ^{13}C-NMR (C_6D_6, 200 MHz): 22.27 (s, CMe_3), 23.85 (s, CH_3). MS (CI_{neg}, NH_3, 36 °C): 658 (25) [$^tBu_3Sb_4^-$], 415 (30) [$^tBu_3Sb_2^-$], 359 (100) [$^tBu_2Sb_2^-$].

3.3. *catena*-$Mes_2Sb(SbPh)_nSbMes_2$ (**4**: $n=1$, **5**: $n=2$)

A solution of 0.28 g (1.0 mmol) $PhSbCl_2$ in 60 ml of THF was added dropwise to a solution of 0.82 g (2.3 mmol) Mes_2SbLi in 40 ml THF at −70 °C. The solution mixture was stirred 1 h at −70 °C and then allowed to warm slowly to r.t. Thereafter, the solvent was removed in vacuo and the residue extracted with 100 ml of petroleum ether. The orange petroleum ether solution was reduced to 10 ml, combined with Al_2O_3 (1 g), dried to a flowing powder under reduced pressure and placed on a chromatography column (8×2 cm, Al_2O_3, activity level II). With petroleum ether/toluene (16/4) an orange broad fraction was eluted. Removal of the solvent gives 0.2 g of a mixture of 16% of *catena*-$Mes_2SbSb(Ph)SbMes_2$ and 4% of *catena*-$Mes_2Sb(Sbh)_2SbMes_2$ as an orange oil. ^1H-NMR (C_6D_6, 200 MHz): *catena*-$Mes_2Sb(SbPh)_2SbMes_2$: 2.03 (s, 6H, CH_3-*p*), 2.12 (s, 6H, CH_3-*p*), 2.29 (s, 12H, CH_3-*o*), 2.54 (s, 12H, CH_3-*o*), 6.62 (s, 4H, C_6H_2-*m*), 6.77 (s, 4H, C_6H_2-*m*), 6.98–7.10 (m, 6H, SbC_6H_5-*m*+*p*), 7.40–7.45 (m, 4H, SbC_6H_5-*o*). *catena*-$Mes_2SbSbPhSbMes_2$: 2.06 (s, 6H, CH_3-*p*), 2.10 (s, 6H, CH_3-*p*), 2.32 (s, 12H, CH_3-*o*), 2.47 (s, 12H, CH_3-*o*), 6.65 (s, 4H, C_6H_2-*m*), 6.73 (s, 4H, C_6H_2-*m*), 6.98–7.10 (m, 3H, SbC_6H_5-*m*+*p*), 7.65–7.70 (m, 2H, SbC_6H_5-*o*). MS (EI, 70 eV, 136 °C): 436 (46) [Mes_2PhSb^+], 359 (10) [Mes_2Sb^+], 316 (58) [$MesPhSb^+$], 195 (100) [$MesSb^+$], 119 (66) [Mes^+], 77 (16) [Ph^+].

3.4. Reaction of $MeSbCl_2$ and R_2SbBr with Mg ($R = CH_2SiMe_3$)

To 0.35 g (14.58 mmol) magnesium filings activated with 0.5 ml 1,2-dibromomethane were added simultaneously 5.43 g (14.44 mmol) $(Me_3SiCH_2)_2SbBr$ in 35 ml THF and 1.5 g (7.21 mmol) $MeSbCl_2$ in 15 ml THF making use of two dropping funnels. The reaction mixture was stirred for 2 h at r.t. until the magnesium had reacted. Thereafter, the solvent was removed in vacuo and the black remaining product mixture was washed with 3×100 ml petroleum ether, giving an orange solution. During the extraction from the orange petroleum ether solution a black solid product precipitate and the solution becomes yellow. 2.77 g (65%) of a yellow–orange oil and 0.31 g of a black powder was obtained. ^1H-NMR (C_6D_6, 200 MHz): $[(Me_3SiCH_2)_2Sb]_2$: 0.17 (s, 36 H, $(CH_3)_3Si$), AB spin system with A: 0.67, B: 0.97 (8 H, CH_2, $^2J_{HH} = 13$ Hz). MS (EI, 70 eV, 238 °C) black product: 546 (1.75) [$Me_4Sb_4^+$], 531 (1.5) [$Me_3Sb_4^+$], 501 (1.8) [$MeSb_4^+$], 410 (100) [$Me_3Sb_3^+$], 395 (69) [$Me_2Sb_3^+$], 365 (54) [Sb_3^+], 304 (62) [$Me_4Sb_2^+$], 289 (34) [$Me_3Sb_2^+$], 274 (19) [$Me_2Sb_2^+$], 259 (26) [$MeSb_2^+$], 244 (20) [Sb_2^+], 166 (11) [Me_3Sb^+], 151 (100) [Me_2Sb^+].

3.5. *cyclo*-[Cr(CO)$_4$(Ph$_2$Sb–SbPh–SbR–SbPh$_2$)] (R = CH$_2$SiMe$_3$) (**8**)

The reaction of a mixture of 0.37 g (0.35 mmol) $(Me_3SiCH_2Sb)_5$ and 0.49 g (0.88 mmol) $(Ph_2Sb)_2$ with 0.22 g (0.88 mmol) [nbdCr(CO)$_4$] in 20 ml of toluene and the work-up procedures were performed as already reported [4]. However, the separation of the reaction products by column chromatography (Al_2O_3, activity level III, 17 × 2 cm) afforded the elution with petroleum ether/toluene (3/1) of a orange fraction, from which after removal of the solvent under reduced pressure 0.023 g (2.3%) of **8** were obtained as yellow microcrystalline solid. M.p. 166 °C. HRMS (EI, 70 eV): 1123.79599 (Calc. 1123.79489 amu, $C_{38}H_{36}O_4SiCr^{52}Sb_2^{121}Sb_2^{123}$, M^+). ^{1}H-NMR (C_6D_6, 200 MHz): −0.16 (s, 9H, $(CH_3)_3Si$), AB spin system with A: −0.02, B: 0.53 (2H, CH_2, $^2J_{HH} = 12.9$ Hz), 6.47–6.63 (m, 3H, SbC_6H_5-*m*+*p*), 6.72–6.76 (m, 2H, SbC_6H_5-*o*), 6.93–7.09 (m, 12H, Sb$(C_6H_5)_2$-*m*+*p*), 7.64–8.10 (m, 8H, Sb$(C_6H_5)_2$-*o*). ^{13}C-NMR (C_6D_6, 50 MHz): −9.22 (s, CH_2), 0.34 (s, $(CH_3)_3Si$), 126.3 (s, C_6H_5-*ipso*), 129.32–129.79 (m, C_6H_5-*m*+*p*), 134.15, 134.52, 134.74, 135.14 (s, C_6H_5-*ipso*), 136.16, 136.27, 136.32, 136.69, 138.40 (s, C_6H_5-*o*), 220.40 (s, CO_{eq}), 221.39 (s, CO_{eq}), 233.98 (s, CO_{ax}). MS (EI, 70 eV, 214 °C): 1124 (5) [M^+], 1012 (52) [M^+ − 4CO], 604 (8) [$Ph_4Sb_2Cr^+$], 552 (38) [$Ph_4Sb_2^+$], 327 (6) [Ph_2SbCr^+], 275 (60) [Ph_2Sb^+], 154 (100) [Ph_2^+], 135 (35) [$PhSi(CH_3)_3^+$], 77 (29) [Ph^+], 52 (17) [Cr^+]. IR (toluene): 2279 s, 2002 vs, 1907 vs cm^{-1} (ν(CO)).

4. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC-201825 for compound **6**·C_6H_6 and CCDC-201826 for compound **8**. Copies of this information can be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank Prof. Dr C.S. Silvestru from the Babes-Bolyai University in Cluj-Napoca, Romania for helpful discussions and the University Bremen for financial support.

References

[1] H.J. Breunig, R. Rösler, Chem. Soc. Rev. 29 (2000) 403 (and references cited therein).
[2] S. Roth, One-Dimensional Metals, Wiley-VCH, Weinheim, 1999.
[3] M. Ates, H.J. Breunig, K. Ebert, S. Gülec, R. Kaller, M. Dräger, Organometallics 11 (1992) 145.
[4] H.J. Breunig, I. Ghesner, E. Lork, Organometallics 20 (2001) 1360.
[5] M. Baudler, G. Reuschenbach, D. Koch, B. Carlsohn, Chem. Ber. 113 (1980) 1264.
[6] E. Urnezius, K.-C.h. Lam, A.L. Rheingold, J.D. Protasiewicz, J. Organomet. Chem. 630 (2001) 193.
[7] G. Johannes, O. Stelzer, E. Unger, Chem. Ber. 108 (1975) 1259.
[8] O. Stelzer, E. Unger, V. Wray, Chem. Ber. 110 (1977) 3430.
[9] A.L. Rheingold, J.E. Lewis, J.M. Bellama, Inorg. Chem. 12 (1973) 2845.
[10] O. Mundt, H. Riffel, G. Becker, A. Simon, Z. Naturforsch. 39B (1984) 317.
[11] H.J. Breunig, M.E. Ghesner, E. Lork, J. Organomet. Chem. 660 (2002) 167.
[12] K. Issleib, B. Hamann, L. Schmidt, Z. Anorg. Allg. Chem. 339 (1965) 298.
[13] H.J. Breunig, T. Severengiz, Z. Naturforsch. 37B (1982) 395.
[14] H.J. Breunig, R. Kaller, A. Silvestru, Phosphorus Sulfur 91 (1994) 165.
[15] A.L. Rheingold, P. Chondhury, J. Organomet. Chem. 128 (1977) 155.
[16] H.J. Breunig, W. Fichtner, T.P. Knobloch, Z. Anorg. Allg. Chem. 445 (1978) 215.
[17] J.v. Seyer, G. Huttner, Cryst. Struct. Commun. 9 (1980) 1099.
[18] H.J. Breunig, J. Pawlik, Z. Anorg. Allg. Chem. 621 (1995) 817.
[19] G. Balazs, H.J. Breunig, in: M. Gielen, R. Willem, B. Wrackmeyer (Eds.), Unusual Structures and Physical Properties in Organometallic Chemistry, Wiley, Chichester, 2002, p. 387.
[20] D.G. Hendershot, A.D. Berry, J. Organomet. Chem. 449 (1993) 119.
[21] H. Althaus, Ph.D. Thesis, Universität Bremen, 2000.
[22] N. Nunn, D.B. Sowerby, D.M. Wesolek, J. Organomet. Chem. 251 (1983) C45.
[23] (a) A.H. Cowley, R.A. Jones, C.M. Nunn, D.E. Westmoreland, Angew. Chem. 101 (1989) 1089;
(b) A.H. Cowley, R.A. Jones, C.M. Nunn, D.E. Westmoreland, Angew. Chem. Int. Ed. Engl. 28 (1989) 1018.