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Journal of Organometallic Chemistry 585 (1999) 285–289

Journal of Organometallic Chemistry

The crystal structure of a trinuclear anion, $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ formed by reaction of *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$ with potassium, and the four-membered rings, *cyclo*-$(t\text{-Bu}_4\text{E}_n\text{Sb}_{4-n})$ ($\text{E} = \text{P}$, $n = 0–3$; $\text{E} = \text{As}$, $n = 0–2$)

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Received 4 March 1999; received in revised form 13 April 1999

Abstract

t-BuSbCl$_2$ and ECl$_3$ react with magnesium in tetrahydrofuran (THF) to give *cyclo*-$(t\text{-Bu}_4\text{E}_n\text{Sb}_{4-n})$ ($\text{E} = \text{P}$, $n = 0–3$; $\text{E} = \text{As}$, $n = 0–2$). Reduction of *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$ with potassium in THF followed by addition of $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$ gives $[\text{K}\{(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}\}_2][(t\text{-Bu}_2\text{Sb})_2\text{Sb}]$. The crystal structure of this salt is reported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Antimony; Phosphorus; Arsenic; Group 15; Crystal structure

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1. Introduction

In course of investigations of organometallic compounds with antimony–antimony bonds [1], we became interested in the syntheses of polycyclic organostibanes [2] and in the reactivity of monocycles. For the present study we chose the *tert*-butyl substituent as protecting group and report here on dehalogenation reactions of t-BuSbCl$_2$ and ECl$_3$ yielding heteroatomic four-membered rings, *cyclo*-$(t\text{-Bu}_4\text{E}_n\text{Sb}_{4-n})$ ($\text{E} = \text{P}$, $n = 0–3$; $\text{E} = \text{As}$, $n = 0–2$) instead of polycycles. The cleavage of *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$ with K in the presence of $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$, giving a solvated potassium salt with the anion $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$, is also presented. Common features of these unexpected reactions are the migrations of the *tert*-butyl groups. The mobility of alkyl groups is not unusual in the chemistry of organoantimony compounds and was mentioned even for the first synthesis reported for *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$ [3]. Migrations indicate preferences for the structures formed.

2. Results and discussion

2.1. Formation of heterocycles by reactions of t-BuSbCl$_2$ and ECl$_3$ ($\text{E} = \text{P}$, As) with magnesium

It is known that reactions of t-BuECl$_2$ and ECl$_3$ ($\text{E} = \text{P}$, As) with magnesium in tetrahydrofuran (THF) lead to polycyclic phosphanes [4], or arsaphosphanes [5]. Four-membered rings, *cyclo*-$(t\text{-Bu}_4\text{E}_4)$, were obtained as side products [5].

We found that the reaction of t-BuSbCl$_2$ and PCl$_3$ (3:1 molar ratio) in boiling THF with excess magnesium did not give polycycles. Instead, the *tert*-butyl groups migrated from antimony to phosphorus and four membered rings, *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$, *cyclo*-$(t\text{-Bu}_4\text{PSb}_3)$, *cyclo*-$(t\text{-Bu}_4\text{P}_2\text{Sb}_2)$, and *cyclo*-$(t\text{-Bu}_4\text{P}_3\text{Sb})$ were obtained as a mixture of yellow crystals in a 1.6:1.3:2.2:1.0 molar ratio.

$$t\text{-BuSbCl}_2,\ \text{PCl}_3 \underset{-\text{MgCl}_2}{\overset{+\text{Mg}}{\rightarrow}} \textit{cyclo}\text{-}(t\text{-Bu}_4\text{P}_n\text{Sb}_{4-n})$$

$$(n = 0 - 3)$$

The relative yields indicate a random distribution of the *tert*-butyl groups between phosphorus and antimony rather than preferences for the formation of specific heterocyles. Attempts to isolate specific hetero-

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PII: S0022-328X(99)00238-7

cycles with reasonable effort by sublimation, by chromatography or by variation of the stoichiometry failed in our hands. As signals of *t*-BuPCl_2 emerge in the ^{1}H-NMR spectra of *t*-BuSbCl_2 and PCl_3 in C_6D_6 a few minutes after mixing the halides, it is probable, that the migration of the *tert*-butyl groups occurs before the reduction.

The four-membered rings were characterized by mass spectrometry and by ^{1}H- and ^{31}P-NMR spectroscopy. *cyclo*-(*t*-Bu_4PSb_3) is a novel compound; *cyclo*-(*t*-Bu_4P_3Sb) and *cyclo*-(*t*-$Bu_4P_2Sb_2$) have been described before [6]. The *cyclo*-(*t*-$Bu_4P_2Sb_2$) isomer with alternating P–Sb bonds [6] was not observed in the experiments described here.

In an analogous procedure mixtures of *t*-BuSbCl_2 and $AsCl_3$ (3:1 molar ratio) were reduced with Mg in THF. Instead of polycyclic arsastibanes, mainly *cyclo*-(*t*-Bu_4Sb_4), *cyclo*-(*t*-Bu_4AsSb_3) and *cyclo*-(*t*-$Bu_4As_2Sb_2$) were obtained in a 25:8:1 molar ratio.

$$t\text{-BuSbCl}_2,\ \text{AsCl}_3 \xrightarrow[-\text{MgCl}_2]{+\text{Mg}} cyclo\text{-}(t\text{-Bu}_4\text{As}_n\text{Sb}_{4-n})$$

$$(n = 0 - 2)$$

The Sb_4 ring and the novel monoheterocyclic arsastibanes were identified by ^{1}H-NMR spectroscopy and by mass spectrometry. It is uncertain which of the two isomers of *cyclo*-(*t*-$Bu_4As_2Sb_2$) was formed. Related to the novel arsastibanes are arsastibenes, RAs = SbR [7], and As/Sb analogues of Salvarsan [8].

Searching for polycycles we have also investigated reactions of *t*-BuSbCl_2 and $SbCl_3$ or $BiCl_3$ with Mg in THF. Both reactions gave (*t*-Bu_4Sb_4) as the only cyclic product identified.

2.2. Reaction of cyclo-(t-Bu_4Sb_4) with potassium in THF in presence of ($Me_2NCH_2CH_2$)$_2$NMe

Potential synthons for selective syntheses of *cyclo*-(*t*-$Bu_4E_nSb_{4-n}$) (E = P, As; $n = 1–2$) are linear dianions, $[t\text{-Bu}_n\text{Sb}_n]^{2-}$ ($n = 2–4$), which should be accessible by reactions of *cyclo*-(*t*-Bu_4Sb_4) with alkali metals. Analogous reactions are well known in the chemistry of phosphorus or arsenic rings [4,9].

There are only few reports on the reduction of cyclostibanes. Issleib and Balszuweit described the reduction of *cyclo*-(Ph_6Sb_6) with appropriate amounts of sodium in liquid ammonia to give solutions of $Na_2(PhSb)_2$ or Na_2(PhSb) [10]. $[t\text{-Bu}_2\text{Sb}_2]^{2-}$ was formed in solution by electrochemical methods [11]. Earlier attempts to isolate products of the cleavage of *cyclo*-(*t*-Bu_4Sb_4) with K in THF in the presence of 18-crown-6 failed however [11].

We have re-investigated the reaction of *cyclo*-(*t*-Bu_4Sb_4) with potassium in THF using (Me_2NCH_2-CH_2)$_2$NMe as ligand for the potassium cation [12] and report here the formation of red crystals of the monoanionic triantimonide, $[\text{K}\{(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}\}_2][(t\text{-Bu}_2\text{Sb})_2\text{Sb}]$. A linear dianion was not obtained.

$$(t\text{-Bu}_4\text{Sb}_4) + \text{K} + 2\text{L} \rightarrow [\text{K(L)}_2][(t\text{-Bu}_2\text{Sb})_2\text{Sb}] + \text{Sb}$$

$$\text{L} = (\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$$

The red crystals of the triantimonide are sensitive towards air and moisture. They decompose at room temperature even in an inert atmosphere. An X-ray structure analysis was carried out at 173 K. The crystals contain amine coordinated potassium cations and $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ anions. The atomic coordinates and the equivalent isotropic displacement coefficients are given in Table 1, crystallographic details are given in Table 2. The cations are hexacoordinated through the nitrogen atoms of two tridentate ($Me_2NCH_2CH_2$)$_2$NMe ligands. They are well separated from the anions. The structure of the anions is depicted in Fig. 1.

The anions consist of bent Sb_3 chains with two *tert*-butyl groups bonded to each of the terminal antimony atoms. The central antimony atom is two coordinated and free of organic substituents. $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ is the second representative of structures of the $[(\text{R}_2\text{Sb})_2\text{Sb}]^-$ type. The analogous phenyl derivative, $[(\text{Ph}_2\text{Sb})_2\text{Sb}]_2^-$, was formed as Li(12-crown-4) salt in the course of an unspecific reaction of Ph_3Sb with Li [13].

The mean Sb–Sb bond length in $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ is 276.5 pm. Similar values have been found for $[(\text{Ph}_2\text{Sb})_2\text{Sb}]^-$ (276.1 pm [13]), Sb_4^{2-} (275 pm [14]) or CpMo$(CO)_2Sb_3$ (274.9 pm [15]). These distances are significantly shorter than the Sb–Sb single bond lengths in Ph_2Sb–$SbPh_2$ (283.7 [16]), (*t*-BuSb)$_4$ (281.7 pm [17]) or $[\text{Me}_2\text{Sb–(Me}_2\text{)Sb–SbMe}_2)]^+$ (282.0 pm, [18]) but longer than the Sb–Sb double bond in RSb = SbR, R = 2,4,6-$[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{C}_6\text{H}_2$ (264.2 pm [19]). The relatively short Sb–Sb bond in $[(\text{Ph}_2\text{Sb})_2\text{Sb}]^-$ has been related to possible (p_π–d_π) bonding [13]. A similar explanation might account for $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$. The Sb–Sb–Sb bond angle in $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ is 86.32 (3)°. This is even more acute than in $[(\text{Ph}_2\text{Sb})_2\text{Sb}]^-$ (88.8°). The C–Sb–C angles in $(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ (104.2 (2)°) and $[(\text{Ph}_2\text{Sb})_2\text{Sb}]^-$ (92.7°) reflect the different sterical demand of the organic substituents. The distances between the terminal antimony atoms in $[(\text{R}_2\text{Sb})_2\text{Sb}]^-$ (R = *t*-Bu, 376.3 (5) pm; R = Ph, 386.4 pm) indicate weak bonding interactions because they are shorter than the sum of the van der Waals radii of two antimony atoms (440 pm). For the description of the conformation of $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]^-$ the dihedral angles Φ (Sb–Sb–Sb–lp), where lp denotes the (assumed) direction of the lone pair of electrons at one of the terminal antimony atoms, are used [1]. For the *syn* conformation, Φ is close to 0° but close to 180° for the *anti* conformation. With $\Phi_1 = 7.23°$ and $\Phi_2 = 24.04°$ as calculated from the C–Sb–Sb–Sb torsion angles given under Fig. 1, the conformation of $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]$ is close to *syn–syn*.

The constitution of the triantimonide shows that the reduction of *cyclo*-$(t\text{-Bu}_4\text{Sb}_4)$ with potassium in boiling THF is a complicated multistep reaction involving cleavage not only of Sb–Sb bonds but also of Sb–C bonds as well as migration of *tert*-butyl groups. The formation of both species, $[(\text{R}_2\text{Sb})_2\text{Sb}]^-$ (R = *t*-Bu, Ph) under scrambling conditions indicates a distinguished stability of this type of structure, which makes these anions interesting as ligands for coordination compounds or precursors of organoantimony compounds such as tristibanes, $(\text{R}_2\text{Sb})_2\text{SbR}$ or antimony star molecules, $(\text{R}_2\text{Sb})_3\text{Sb}$.

Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[\text{K}\{(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}\}_2]$ $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]$ [a]

	x	*y*	*z*	U_{eq}
Sb(1)	3666(1)	1031(1)	4306(1)	26(1)
Sb(2)	5073(1)	171(1)	5102(1)	37(1)
Sb(3)	3304(1)	−758(1)	4817(1)	27(1)
K(1)	9051(1)	269(1)	7457(1)	37(1)
N(1)	8355(4)	−975(3)	6688(2)	42(1)
N(2)	9723(4)	−1024(2)	7995(2)	39(1)
N(3)	9234(4)	112(3)	8848(2)	39(1)
N(4)	7043(5)	1199(3)	7296(3)	49(1)
N(5)	9045(6)	1286(4)	6485(4)	77(2)
N(6)	11249(6)	1075(3)	7443(3)	55(1)
C(1)	4842(5)	1306(3)	3575(3)	36(1)
C(2)	3677(5)	1928(3)	4938(3)	41(1)
C(3)	2708(5)	−895(3)	5796(3)	38(1)
C(4)	4346(5)	−1675(3)	4687(3)	43(1)
C(11)	6035(5)	1567(4)	3873(3)	52(2)
C(12)	4243(7)	1807(3)	3100(3)	56(2)
C(13)	5007(6)	656(3)	3223(3)	48(2)
C(21)	3260(8)	2528(3)	4523(4)	72(2)
C(22)	4847(7)	2076(4)	5329(4)	71(2)
C(23)	2788(7)	1768(4)	5389(3)	61(2)
C(31)	1979(6)	−283(3)	5870(3)	54(2)
C(32)	1913(7)	−1498(3)	5767(4)	70(2)
C(33)	3676(7)	−947(5)	6345(3)	81(3)
C(41)	5286(8)	−1809(4)	5249(4)	81(3)
C(42)	4884(8)	−1563(4)	4076(4)	71(2)
C(43)	3541(8)	−2273(3)	4603(4)	72(2)
C(51)	7151(6)	−965(5)	6833(4)	71(2)
C(52)	8351(7)	−967(4)	5989(3)	58(2)
C(53)	8965(6)	−1563(3)	6948(3)	50(2)
C(54)	9152(6)	−1604(3)	7676(3)	51(2)
C(55)	10891(6)	−954(5)	7813(3)	62(2)
C(56)	9777(6)	−1081(3)	8699(3)	49(2)
C(57)	10035(5)	−429(4)	9062(2)	46(1)
C(58)	9561(7)	697(4)	9241(3)	58(2)
C(59)	8028(6)	−54(4)	8897(4)	63(2)
C(61)	5939(8)	873(4)	7191(6)	93(3)
C(62)	7130(11)	1599(5)	7865(5)	105(4)
C(63)	7142(10)	1612(7)	6737(5)	132(6)
C(64)	7943(11)	1669(7)	6412(6)	172(8)
C(65)	9065(9)	872(5)	5907(5)	94(3)
C(66)	10051(10)	1719(4)	6572(4)	85(3)
C(67)	11195(8)	1392(4)	6815(4)	73(2)
C(68)	11176(10)	1534(5)	7959(4)	85(3)
C(69)	12378(7)	728(4)	7591(4)	73(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2
Crystal data and structure refinement for $[\text{K}\{(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}\}_2]$ $[(t\text{-Bu}_2\text{Sb})_2\text{Sb}]$

Empirical formula	$C_{34}H_{82}KN_6Sb_3$
Formula weight	979.41
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	
a (Å)	11.521(2)
b (Å)	20.051(4)
c (Å)	20.861(8)
α (°)	90
β (°)	97.58(4)
γ (°)	90
Volume ($Å^3$)	4777(2)
Z	4
Density (calculated) (Mg m^{-3})	1.362
Absorption coefficient (mm^{-1})	1.798
F(000)	2000
Crystal size (mm^3)	0.80 × 0.50 × 0.30
θ range for data collection	2.68–27.55°
Index ranges	$-14 \leq h \leq 1$, $-15 \leq k \leq 13$, $-27 \leq l \leq 27$
Reflections collected	11318
Independent reflections	6246 [$R_{int} = 0.0379$]
Completeness to $\theta = 27.55°$	95.4%
Absorption correction	Empirical
Max. and min. transmission	0.6146 and 0.3273
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6246/2/423
Goodness-of-fit on F^2	1.038
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0261$, $wR_2 = 0.0617$
R indices (all data)	$R_1 = 0.0306$, $wR_2 = 0.0639$
Absolute structure parameter	0.36(3)
Extinction coefficient	0.00007(3)
Largest diff. peak and hole (e $Å^{-3}$)	0.721 and −0.637

3. Experimental

All the experiments were performed in an argon atmosphere using dried solvents distilled under argon. The NMR spectra were recorded on a Bruker AM 360 instrument operating at 360 MHz for ^{1}H and 146 MHz for ^{31}P. For the mass spectrometry a Finnigan MAT 8222 instrument was used. Only the most intense signals of a group of signals corresponding to the theoretical distribution are presented here. The details of the crystal structure determination and refinement are given in Table 2. Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). For this purpose the crystal was attached with Kel-F-oil to a glass fiber and cooled under a nitrogen stream to 173 K. The structure was solved, after Lp- and absorption correction, by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used [20]. The drawings were created with the XP-Program of the SHELXTL program system [21].

3.1. Preparation of *cyclo*-(t-$Bu_4P_nSb_{4-n}$) ($n = 0$–3)

A solution of t-BuSbCl$_2$ (18.80 g, 73.67 mmol) and PCl$_3$ (3.37 g, 24.54 mmol) in THF (100 ml) was added under stirring to activated (with C$_2$H$_4$Br$_2$) Mg turnings (3.63 g, 149.35 mmol) in boiling THF (20 ml). The addition was completed after 30 min and the dark brown reaction mixture was stirred for further 45 min with reflux. The solvent was removed in vacuum and the solid residue was extracted with petroleum ether (3 × 200 ml). The petroleum ether extracts were combined, filtered and reduced to 20 ml. Upon cooling at -28°C yellow crystals (7.27 g) formed and were filtered out. Corresponding to the ^{1}H-NMR spectrum, they consisted of a mixture of *cyclo*-(t-Bu$_4$Sb$_4$), *cyclo*-(t-Bu$_4$PSb$_3$), *cyclo*-(t-Bu$_4$P$_2$Sb$_2$), and *cyclo*-(t-Bu$_4$P$_3$Sb) in a 1.6:1.3:2.2:1.0 molar ratio.

^{1}H-NMR (C$_6$D$_6$): *cyclo*-(t-Bu$_4$Sb$_4$): $\delta = 1.56$ (s) [16]; *cyclo*-(t-Bu$_4$PSb$_3$): $\delta = 1.30$ (d, 9H, $^3J_{P,H} = 12.97$ Hz, t-BuP), 1.51 (s, 18H, t-BuSb(P)Sb), 1.60 (s, 9H, t-BuSbSb$_2$); *cyclo*-(t-Bu$_4$P$_2$Sb$_2$): $\delta = 1.29$ (d, 18H, $^3J_{P,H} = 12.97$ Hz, t-BuP), 1.55 (s, 18H, t-BuSb); *cyclo*-(t-Bu$_4$P$_3$Sb): $\delta = 1.23$ (d, 9H, $^3J_{P,H} = 12.97$ Hz, t-BuPP$_2$), 1.27 (d, 18H, $^3J_{P,H} = 13.7$ Hz, t-BuP(P)Sb), 1.47 (s, 9H, t-BuSb); ^{31}P-NMR (C$_6$D$_6$): *cyclo*-(t-Bu$_4$PSb$_3$): $\delta = -80.0$ (s); *cyclo*-(t-Bu$_4$P$_2$Sb$_2$): $\delta = -48.2$ (s), ($\delta = -54.5$ in pentane at -60° [6]); *cyclo*-(t-Bu$_4$P$_3$Sb): $\delta = -75.3$ (d, 2P, $^1J_{P,P} = 169.2$ Hz, PP$_2$), -31.2 (t, 1P, $^1J_{P,P} = 169.2$ Hz, P(P)Sb), ($\delta = -35.7$; -82.1; $^1J_{P,P} = 169,2$ Hz in pentane at -60° [6]); MS (EI, 70 eV): *cyclo* $-$ (t $-$ Bu$_4$Sb$_4$): $m/z = 716$ [M$^+$], 659, 603, 546, 489; *cyclo*-(t-Bu$_4$PSb$_3$): $m/z = 627$ [M$^+$], 567, 511, 454, 397; *cyclo*-(t-Bu$_4$P$_2$Sb$_2$): $m/z = 534$ [M$^+$], 477, 421, 365, 309; *cyclo*-(t-Bu$_4$P$_3$Sb): $m/z = 442$ [M$^+$], 385, 329, 273, 217.

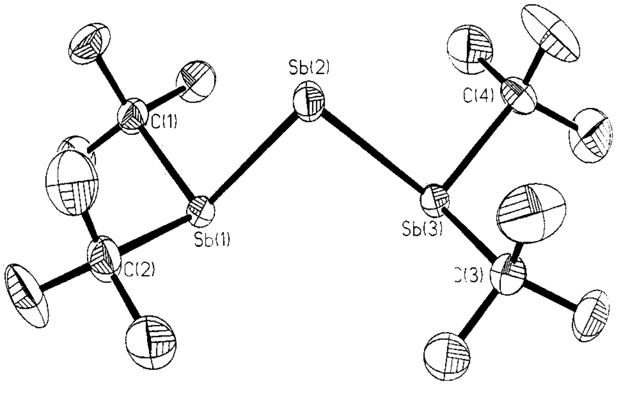

Fig. 1. Structure of the (t-Bu$_2$Sb)$_2$Sb$^-$ anion. Selected distances [pm] and angles [°]: Sb(1)–Sb(2) 276.43(9), Sb(2)–Sb(3) 276.69(7), Sb(1)–C(1) 223.9(5), Sb(2)–C(2) 222.9(6), Sb(3)–C(3) 225.5(5), Sb(3)–C(4) 223.2(5), Sb(1)–Sb(2)–Sb(3) 86.23(3), C(1)–Sb(1)–Sb(2) 101.70(15), C(2)–Sb(1)–Sb(2) 101.03(16), C(2)–Sb(1)–C(1) 104.3(2), C(3)–Sb(3)–Sb(2) 101.03(15), C(4)–Sb(3)–Sb(2) 100.85(16), C(4)–Sb(3)–C(3) 104.0(2), C(1)–Sb(1)–Sb(2)–Sb(3) −122.75(14), C(2)–Sb(1)–Sb(2)–Sb(3) −129.98(15), Sb(1)–Sb(2)–Sb(3)–C(3) −114.58(15), Sb(1)–Sb(2)–Sb(3)–C(4) 138.62(16)

3.2. Preparation of *cyclo*-(t-$Bu_4As_nSb_{4-n}$) ($n = 0$–2)

A solution of t-BuSbCl$_2$ (8.03 g, 32.15 mmol) and AsCl$_3$ (1.95 g, 10.76 mmol) in THF (70 ml) was added under stirring to activated (with C$_2$H$_4$Br$_2$) Mg turnings (1.66 g, 68.3 mmol) in boiling THF (20 ml). The addition was completed after 30 min and the dark brown reaction mixture was stirred for further 60 min with reflux. The solvent was removed in vacuum and the solid residue was extracted with petroleum ether (3 × 200 ml). The petroleum ether extracts were combined, filtered and reduced to 20 ml. Upon cooling at -70°C yellow crystals (3.08 g) formed and were isolated by decanting of the supernatant solution. The crystals consisted of a mixture of *cyclo*-(t-Bu$_4$Sb$_4$), *cyclo*-(t-Bu$_4$AsSb$_3$), and *cyclo*-(t-Bu$_4$As$_2$Sb$_2$) in a 25:8:1 molar ratio (^{1}H-NMR).

^{1}H-NMR (C$_6$D$_6$): *cyclo*-(t-Bu$_4$AsSb$_3$): $\delta = 1.49$ (s, 9H, t-BuAs), 1.52 (s, 18H, t-BuSb(As)Sb), 1.59 (s, 9H, t-BuSbSb$_2$); *cyclo*-(t-Bu$_4$As$_2$Sb$_2$): $\delta = 1.31$ (s, 18H, t-BuAs), 1.55 (s, 18H, t-BuSb); MS (EI, 70 eV): *cyclo*-(t-Bu$_4$Sb$_4$): $m/z = 716$ [M$^+$], 659, 603, 546, 489; *cyclo*-(t-Bu$_4$AsSb$_3$): $m/z = 668$ [M$^+$], 611, 555, 499, 441; *cyclo*-(t-Bu$_4$As$_2$Sb$_2$): $m/z = 622$ [M$^+$], 565, 509, 453.

3.3. Preparation of [K{($Me_2NCH_2CH_2)_2NMe$}$_2$][(t-$Bu_2Sb)_2Sb$]

To a solution of *cyclo*-(t-Bu$_4$Sb$_4$) (1.0 g, 1.4 mmol) in THF (40 ml) small pieces of K (0.273 g, 7 mmol) were added and the mixture was stirred with reflux for 1 h. The red–brown solution was filtered through a frit and (Me$_2$NCH$_2$CH$_2$)$_2$NMe (0.88 ml, 4.2 mmol) was added. After stirring the solution at 25°C for 1 h, the volume was reduced to 5 ml by evaporation. Slow cooling of the mixture to -28°C gave red crystals of [K{(Me$_2$NCH$_2$CH$_2$)$_2$NMe}$_2$][(t-Bu$_2$Sb)$_2$Sb] (0.35 g), decomposing at room temperature.

Acknowledgements

The authors gratefully acknowledge financial support from Deutsche Forschungsgemeinschaft and Volkswagen-Stiftung.

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