# One-step synthesis of pentavalent triphenylantimony derivatives $Ph_3Sb(OSiR_3)_2$, $Ph_3Sb(OCH_2CH_2)_2NH$ and $Ph_3Sb(OCH_2CH_2NMe_2)_2$: X-ray molecular structure of $Ph_3Sb(OSiMe_3)_2$

Elena Yu. Ladilina [a],[*], Vladimir V. Semenov [a], Georgii K. Fukin [a], Aleksey V. Gushchin [b],
Viktor A. Dodonov [b], Irina V. Zhdanovich [c], Jean-Pierre Finet [d]

[a] *G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, GSP-445, 49 Tropinin Street, 603950 Nizhny Novgorod, Russian Federation*
[b] *Department of Organic Chemistry, Nizhny Novgorod State University, 23 Gagarin Avenue, 603950 Nizhny Novgorod, Russian Federation*
[c] *Nizhny Novgorod State Medical Academy, 10/1 Minin Square, 603005 Nizhny Novgorod, Russian Federation*
[d] *Faculte des Sciences St-Jyrfme, UMR-CNRS 6517, Aix-Marseille University, 13397 Marseille Cedex 20, France*

## Abstract

Pentavalent bis(triorganosiloxy)triphenylantimony derivatives, $Ph_3Sb(OSiR_3)_2$ (R = Me, Ph), were synthesized by reaction of triphenylantimony with trimethyl- or triphenylsilanol in the presence of *tert*-butylhydroperoxide by the mild reaction conditions (0–5 °C, 2 h). The reaction of triphenylantimony with diethanolamine in the presence of *tert*-butylhydroperoxide gave the cyclic compound $Ph_3Sb(OCH_2CH_2)_2NH$. The mixture of $Ph_3SbO$ and $Ph_3Sb(OCH_2CH_2NMe_2)_2$ was obtained by the reaction of triphenylantimony with 2-(N,N-dimethylamino)ethanol in the presence of *tert*-butylhydroperoxide.
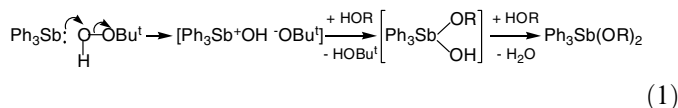© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Antimony(V); Peroxide; Silanols; Ethanolamines; Oxidation; $^1$H, $^{29}$Si NMR spectroscopy

## 1. Introduction

Pentavalent $Ph_3SbX_2$ compounds can be obtained by a one-step oxidative method. This is the reaction of triphenylantimony with OH-containing reagents in the presence of hydrogen peroxide [1] or the organic hydroperoxide [2]. The simplicity of the procedure and mildness of the reaction conditions are the main advantages of this method. This method has been used to prepare a range of Sb(V) compounds by using carboxylic acids [3,4], sulfonic acids [5], glycols [6], diphenols [7], phenylboric acid, silanediols [8], oximes [9,10] and β-diketones [11] as the OH-containing reagents.
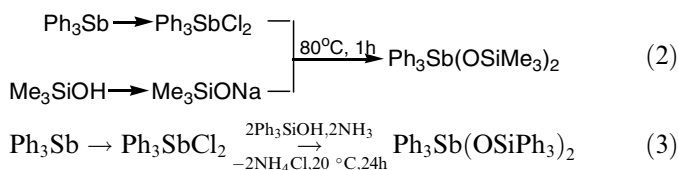
The reaction mechanism $Ph_3Sb$ with OH-containing reagents (ROH) in the presence of $Bu^tOOH$ may be visualized as follows. $Ph_3Sb$ attacks the peroxide oxygen to give a hydroxymetallonium ion [12]. Further deprotonation of OH-containing reagents (ROH) by the strongly basic $Bu^tO^-$ anion produces $Bu^tOH$ and unstable hydroxyalkoxy-derivatives of antimony (V) [11] which is converted into dialkoxy-derivatives of triphenylantimony by means of the OH-group substitution on treatment with ROH.

$$Ph_3Sb\overset{\frown}{\text{:}}\ \underset{H}{O}\text{--}OBu^t \rightarrow [Ph_3Sb^+OH\ ^-OBu^t] \xrightarrow[-\ HOBu^t]{+\ HOR} \left[Ph_3Sb\diagdown{\overset{OR}{\underset{OH}{}}}\right] \xrightarrow[-\ H_2O]{+\ HOR} Ph_3Sb(OR)_2$$
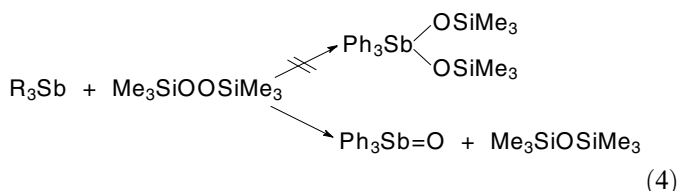
(1)

* Corresponding author. Fax: +7 8312 12 74 97.
  *E-mail address:* llena@iomc.ras.ru (E.Yu. Ladilina).

The *tert*-BuOOH-mediated oxidative method has not been used for the preparation of disiloxytriorganoantimony derivatives, $R_3Sb(OSiR'_3)_2$. The compounds of this type have been synthesized in two or three-step sequences, involving the oxidation of triorganoantimony to triorganoantimony(V) dichloride, followed by reaction with sodium silanolate or with silanol in the presence of ammonia [13,14].

$$Ph_3Sb \longrightarrow Ph_3SbCl_2 \atop Me_3SiOH \longrightarrow Me_3SiONa \Bigg] \xrightarrow[80^\circ C, 1h]{} Ph_3Sb(OSiMe_3)_2 \qquad (2)$$

$$Ph_3Sb \rightarrow Ph_3SbCl_2 \xrightarrow[-2NH_4Cl, 20\ ^\circ C, 24h]{2Ph_3SiOH, 2NH_3} Ph_3Sb(OSiPh_3)_2 \qquad (3)$$

On the other hand, the reaction of triphenylantimony with bis(trimethylsilyl)peroxide afforded only triphenylantimony oxide and hexamethyldisiloxane, but not bis(trimethylsiloxy)triphenylantimony contrary to expectations of authors [2].
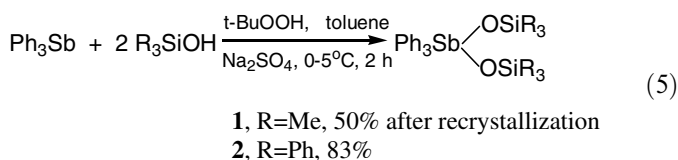
$$R_3Sb\ +\ Me_3SiOOSiMe_3 \atop \nearrow\ Ph_3Sb{\atop\diagdown}^{OSiMe_3}_{OSiMe_3} \atop \searrow\ Ph_3Sb{=}O\ +\ Me_3SiOSiMe_3$$

(4)

In the present paper, we report the reaction of triphenylantimony with Bu$^t$OOH in the presence of organosilanols (trimethylsilanol, triphenylsilanol), or amino-alcohols (diethanolamine and *N,N*-dimethylethanolamine).

## 2. Results and discussion

### 2.1. Reaction of triphenylantimony with silanols in the presence of tert-BuOOH

Oxidation of triphenylantimony by Bu$^t$OOH in the presence of 2 equivalents of trimethylsilanol or triphenylsilanol afforded after stirring during 2 h the bis(trimethylsiloxy)triphenylantimony **1** or bis(triphenylsiloxy)triphenylantimony **2**, respectively. In both cases, the reaction was carried out under cooling to avoid the competitive formation of diorganosiloxanes by dehydration of the silanols.

$$Ph_3Sb\ +\ 2\ R_3SiOH \xrightarrow[Na_2SO_4,\ 0-5^\circ C,\ 2\ h]{t\text{-BuOOH, toluene}} Ph_3Sb{\diagdown}^{OSiR_3}_{OSiR_3}$$

(5)

**1**, R=Me, 50% after recrystallization
**2**, R=Ph, 83%

Both products are stable to air and moisture resistant. These compounds were described by element analysis and melting-point [13,14], and compound **1** – by IR spectroscopy only [13].

The IR, $^1H$ NMR and $^{29}Si$ NMR spectra of the compounds **1** and **2** have been studied. In the IR spectra of these compounds, a difference was observed in the position and intensity of the absorption bands of the Sb–O–Si frag-

ment in the siloxy derivatives **1** and **2**. In compound **1**, the band is wider and more intensive than in compound **2** and it is shifted by 40 cm$^{-1}$ to shorter wavelengths (**1**, $v_{max}(KBr) = 940\ cm^{-1}$; **2**, $v_{max}(KBr) = 980\ cm^{-1}$). This shift results from the more electron-withdrawing effect of the phenyl substituents in Sb–O–SiPh$_3$ compared to the effect of the donor methyl groups of the trimethylsiloxy derivative Sb–O–SiMe$_3$. In the $^1H$ NMR spectrum of **1**, a singlet appears at −0.02 ppm corresponding to the 18 protons of the two trimethylsilyl groups and two multiplets at 7.60 and 8.27 ppm correspond to the 15 protons of the SbPh groups. In the $^1H$ NMR spectrum of Me$_3$SiOSiMe$_3$ and Me$_3$SiOSiPh$_3$, a methyl proton resonance appear at 0.06 and 0.10 ppm [15]. In the $^{29}Si$ NMR spectrum of **1**, the signal appears at 2.4 ppm. This value is very close to that of the signal observed for hexamethyldisiloxane (6.3 ppm) [16]. Thus, the $^1H$ and $^{29}Si$ NMR spectra show the absence of Me$_3$SiO(Ph$_3$)Sb– fragments electron-withdrawing influence on SiMe$_3$ group in compound **1**. Most likely, this fragment is electron-donor. In the $^{29}Si$ NMR spectrum of **2**, a signal appears at −23.9 ppm, a value very close to that of the signal observed for hexaphenyldisiloxane (−18.5 ppm). This reflects the similarity of the electronegativities of antimony and silicon (1.9 and 1.8, respectively, in the Pauling scale [17]).

The compound **1** has been structurally characterized by X-ray analysis which revealed that the antimony atom exhibits trigonal-bipyramidal coordination where the Ph-groups occupy the equatorial positions and the trimethylsiloxy groups occupy the apical positions (Fig. 1 and Table 1). The Sb(1)–C(Ph) distances vary in the range of 2.098(2)–2.113(2)Å and are typical for Sb–Ar distances (2.092–2.137Å [18–20]). The Sb(1)–O(1) and Sb(1)–O(2) bond lengths are close to each other [2.006(2)Å and 2.012(2)Å, respectively]. If we compare the molecular structure of compound **1** with the structures of different Ph$_3$Sb(OR)$_2$ derivatives (Table 2), the most striking difference lies in the lengths of the Sb–O distance that are shorter than the typical Sb–O distance (2.05Å) [21]. Moreover, the order is: SbOTMS < SbOH < SbOMe. In spite of the steric bulk of the trimethylsilyl group, the Sb–O bond is the shortest for the TMS ether (2.009Å). Compared to the normal Sb–O distance of 2.05Å, the percentages of contraction of the Sb–O bond in Ph$_3$Sb(OR)$_2$ derivatives (R = TMS, H, Me), are 2%, 1.5% and 0.9%, respectively. When the Sb–O bond is part of a bidentate system such as in ester compounds Ph$_3$Sb[OC(O)R]$_2$ (R = CPh$_2$OH, CH=CH–Ph, CF$_3$), the bond lengths Sb–O are somewhat longer (2.102–2.156Å [22,23]). The Si(1)–O(1) and Si(2)–O(2) distances are 1.617(2)Å and 1.624(2)Å, respectively and are close to analogous distances found in Sb(OSiMe$_3$)$_5$ · Py and Sb(OSiMe$_3$)$_3$ · Py (1.603–1.657Å [24,25]) complexes. In the three related dihydroxide derivatives Ph$_3$Sb(OR)$_2$ (R = H, Me, TMS), the O–Sb–O angle is practically identical in the dihydroxide and its TMS ether (178.5°), but a slight distortion is induced by the methyl substitution (175.3° for the dimethoxy derivative). The Si(1)O(1)Sb(1)
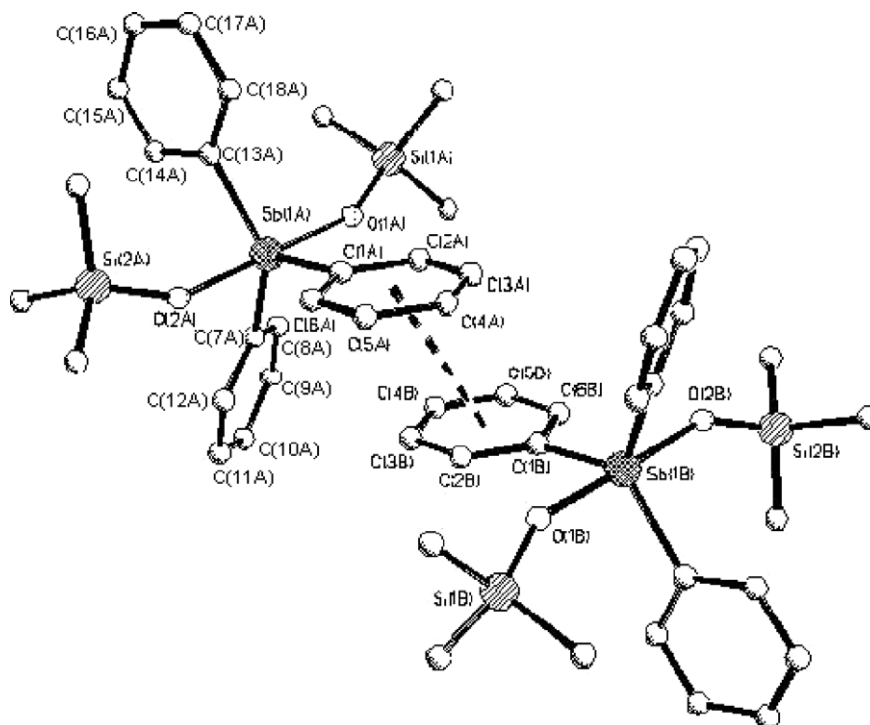
Fig. 1. X-ray molecular structure of compound **1**.

Table 1
Selected bond lengths and bond angles ($\omega$/°) (d/E) for **1**

| Bond lengths (E) | | Bond angles ($\omega$/°) | |
|---|---|---|---|
| Sb(1)–O(1) | 2.006(2) | O(1)Sb(1)O(2) | 178.54(7) |
| Sb(1)–C(7) | 2.098(2) | O(1)Sb(1)C(7) | 90.42(8) |
| Sb(1)–C(1) | 2.113(2) | O(2)Sb(1)C(7) | 90.76(8) |
| Sb(1)–O(2) | 2.012(2) | O(1)Sb(1)C(13) | 89.84(8) |
| Sb(1)–C(13) | 2.110(2) | O(2)Sb(1)C(13) | 88.84(8) |
| Si(1)–O(1) | 1.617(2) | C(7)Sb(1)C(13) | 118.78(9) |
| | | O(1)Sb(1)C(1) | 89.74(8) |
| | | O(2)Sb(1)C(1) | 90.38(8) |
| | | C(7)Sb(1)C(1) | 121.25(9) |
| | | C(13)Sb(1)C(1) | 119.96(9) |
| | | Si(1)O(1)Sb(1) | 153.63(11) |
| | | Si(2)O(2)Sb(1) | 149.04(11) |

Table 2
Comparison of mean distances in some trigonal bipyramidal pentavalent triphenylantimony derivatives

| Compound | $d$(Sb–O)ap (E) | O–Sb–O (°) | Reference |
|---|---|---|---|
| **1** Ph$_3$Sb(OTMS)2 | 2.009 | 178.54 | This work |
| Ph$_3$Sb(OMe)$_2$ | 2.033 | 175.3 | [26] |
| Ph$_3$Sb(OH)$_2$ | 2.021 | 178.5 | [27] |
| Ph$_3$Sb(ON=CHPh)$_2$ | 2.065 | 176.46 | [9] |
| Ph$_3$Sb(ON=CMe$_2$)$_2$ | 2.047 | 176.0 | [9] |
| Ph$_3$Sb(ON=CMeC$_5$H$_4$N-2)$_2$ | 2.068 | 172.78 | [28] |
| Ph$_3$Sb(OAc)$_2$ | 2.130 | 176.1 | [29] |
| Ph$_3$Sb[OCOC(OH)Ph$_2$]$_2$ | 2.223 | 171.98 | [22] |
| Ph$_3$Sb(OCOCF$_3$)$_2$ | 2.134 | 175.5 | [23] |
| Ph$_3$Sb(OCO-thiophenyl-2)$_2$ | 2.120 | 176.68 | [30] |
| Ph$_3$Sb(OCO-pyr-2)$_2$ | 2.142 | 169.9 | [31] |

and Si(2)O(2)Sb(1) angles are close to each other: 153.6(1)° and 149.0(1)°, respectively.

In the crystal lattice, the molecules of compound **1** form dimers due to $\pi$–$\pi$ interaction between the C(1–6) aromatic rings of neighbouring molecules. The distances between the centers of the Ph-rings are 4.057(3)E, and the distances between the planes, in which these rings are disposed, are equal to 3.674(4)E (Fig. 1). Such distances correspond to $\pi$–$\pi$ interactions between aromatic rings [32].

The trigonal bipyramidal structure provides high stability to compound **1**. Indeed, the thermal decomposition of compound **1** proceeded only under harsh conditions (vacuum, 250 °C) to lead to the formation of triphenylantimony oxide and hexamethyldisiloxane, isolated in only a 13% yield after 1 h of treatment.
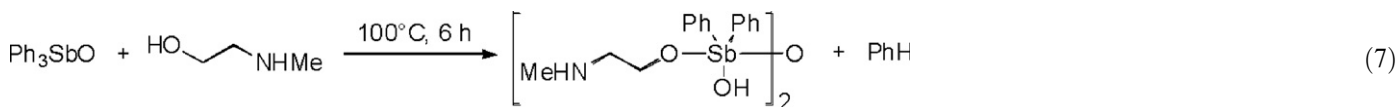
$$Ph_3Sb(OSiMe_3)_2 \xrightarrow{250\,°C,\,Vacuum} Ph_3SbO + Me_3SiOSiMe_3 \quad (6)$$
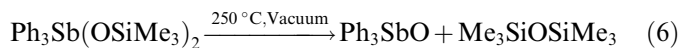
The thermal stability of Ph$_3$Sb(OSiMe$_3$)$_2$ confirms the conclusion that the reaction of Ph$_3$Sb with Me$_3$SiOOSi-Me$_3$, leading to Ph$_3$SbO and Me$_3$SiOSiMe$_3$ under mild conditions, does not involve the intermediate formation of Ph$_3$Sb(OSiMe$_3$)$_2$ [2].
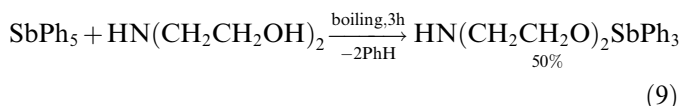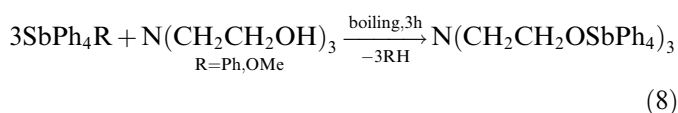
### 2.2. Reaction of triphenylantimony with ethanolamines in the presence of tert-BuOOH

Unlike triorganosilanols, ethanolamines are able to be either mono-, bi-, tri- or tetradentate ligands of antimony(V) with or without participation of the amino-group, respectively. Some of examples of organoantimony compounds containing ethanolamine ligands have been
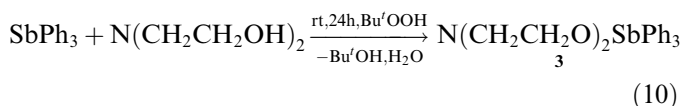
previously reported. Nomura et al. showed that heating of triphenylantimony oxide in *N*-methylaminoethanol or reaction of *N*-methylaminoethanol with $Ph_3Sb(OMe)_2$ prepared in situ results to the formation of bis [(*N*-methyl-2-aminoethoxy)hydroxydiphenyl]antimony oxide [33].

atoms is more pronounced. The proton of the >N-H group appear as a multiplet by reason of the nitrogen atom slow inversion because of intermolecular hydrogen bonds or intramolecular interaction between Sb and N atoms. D. Kraft and M. Wieber [34] establish that heterocycle **3** exist

$$Ph_3SbO \ + \ HO{\diagdown}{\diagup}NHMe \xrightarrow{100°C, 6\,h} \left[ MeHN{\diagdown}{\diagup}O-\overset{\overset{\displaystyle Ph\ \ Ph}{|}}{\underset{\underset{\displaystyle OH}{|}}{Sb}}-O \right]_2 \ + \ PhH \tag{7}$$

Kraft and Wieber [34] used an reaction of pentaphenylstibane and methoxytetraphenylstibane with diethanolamine or triethanolamine to obtain alkoxy derivatives of antimony(V):

$$3SbPh_4R + N(CH_2CH_2OH)_3 \underset{-3RH}{\overset{\text{boiling,3h}}{\xrightarrow{\hspace{1.5cm}}}} N(CH_2CH_2OSbPh_4)_3 \tag{8}$$
$$\underset{R=Ph,OMe}{}$$

$$SbPh_5 + HN(CH_2CH_2OH)_2 \underset{-2PhH}{\overset{\text{boiling,3h}}{\xrightarrow{\hspace{1.5cm}}}} \underset{50\%}{HN(CH_2CH_2O)_2SbPh_3} \tag{9}$$

In the oxidative-addition reaction of triphenylantimony with glycols [6], if the hydroxy groups of the glycol are separated by a sufficient number of carbon atoms, the reaction leads to the formation of polymers. In an extension of this previous work, we investigated the reaction of triphenylantimony with diethanolamine in presence $Bu^tOOH$. Since the OH groups are rather separated from each other, we considered that the reaction products should have a polymer structure. When triphenylantimony was treated with diethanolamine and $Bu^tOOH$ in equimolecular amounts, a white precipitate was formed. Its HPLC analysis showed that the product is in fact a monomeric compound, with a molecular weight corresponding to the eight-membered heterocycle (**3**), 5,5,5-triphenyl-4,6-dioxa-5-stibaperhydroazocine.
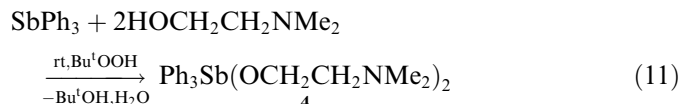
$$SbPh_3 + N(CH_2CH_2OH)_2 \underset{-Bu^tOH,H_2O}{\overset{rt,24h,Bu^tOOH}{\xrightarrow{\hspace{1.5cm}}}} \underset{\mathbf{3}}{N(CH_2CH_2O)_2SbPh_3} \tag{10}$$

The $^1$H NMR spectrum of compound **3** presented signals corresponding to three phenyl groups (multiplet in the range of 7.32–7.76 ppm), methylene groups of an oxygen atom (multiplet at 4.05 ppm) and a nitrogen atom (a widened doublet at 2.76 ppm and a multiplet at 3.19 ppm), and also to >N–H proton (multiplet at 2.97 ppm). Due to the cyclic nonplanar structure, the axial and equatorial protons of methylene groups bound to the nitrogen atom and the oxygen atoms are not equivalent. The protons of the $CH_2O$ groups appear as a multiplet, while the protons of the $CH_2N$ groups appear as two separate signals (axial and equatorial). Hence, it may be concluded that the nonequivalence of the latter hydrogen

in both-conformation. This compound was not studied by IR spectroscopy. Authors suppose that this conformation is stable because of strong intramolecular coordination bond between Sb and N. Nevertheless in the IR spectrum of compound **3** the absorption band of N-H stretching vibrations is in the range of 3150 cm$^{-1}$, typical for associated NH groups. The absence of absorption bands, corresponding to the fragment $R_3HN^+$, indicated that there is no firm strong coordination bond between the atoms of nitrogen and antimony. For the analogous silicon compound, $Ph_2Si(OCH_2CH_2)_2NH$, the presence of a very loose intramolecular interaction is known [34]. The experimental dipole moment of this compound is by far closer to the calculation dipole moment for both-conformer without the Si ← N bond then to the calculation dipole moment for both-conformer with the Si ← N bond [35]. Therefore, the geometry of the both-conformer allows formation of the intramolecular coordination bond, but interaction between Sb and N atoms in compound **3** is very weak.
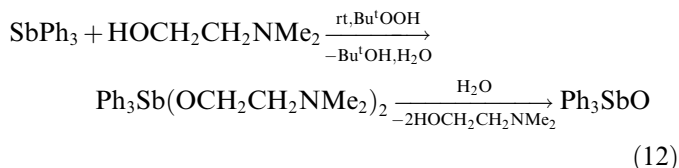
The reaction of triphenylantimony with *N,N*-dimethyl-2-aminoethanol and *tert*-butyl hydroperoxide in a molar ratio 1:2:1 gave a clear viscous liquid, which according data of $^1$H NMR spectroscopy and the HPLC analysis was a mixture of bis(*N,N*-dimethyl-2-aminoethoxy)triphenylantimony (**4**) and $Ph_3SbO$ (~20% mol). We were unable neither to remove triphenylantimony oxid from the final product nor to decrease its amount. Apparently $Ph_3SbO$ is well soluble in compound **4**.

$$SbPh_3 + 2HOCH_2CH_2NMe_2$$
$$\underset{-Bu^tOH,H_2O}{\overset{rt,Bu^tOOH}{\xrightarrow{\hspace{1.5cm}}}} \underset{\mathbf{4}}{Ph_3Sb(OCH_2CH_2NMe_2)_2} \tag{11}$$

In the IR spectrum, absorption bands at 2820, 2775, 2725 cm$^{-1}$ correspond to the stretching vibrations of the methyl groups C-H bonds of the nitrogen atom. Their localization indicates the absence of coordination between the nitrogen atom and the antimony atom, in spite of the high basicity of tertiary amino groups. In this spectrum, four C-H absorption bands (2980, 2945, 2860, 1460 cm$^{-1}$), belonging to $CH_2$ groups, a very intensive absorption band at 1050 cm$^{-1}$, corresponding to the vibrations of the Sb-O-C fragment and a series of bands, corresponding to phenyl substituents vibrations of the antimony atom (3060, 1605,

1580, 1480, 1430, 1070, 830, 700, 455 cm$^{-1}$) were observed. Two absorption bands at 650 and 670 cm$^{-1}$ can be explained by the presence of triphenylantimony oxide, as an impurity.

In the $^1$H NMR spectrum, the signals corresponding to the phenyl groups (a multiplet in the 7.32–7.76 ppm range), methylene groups bound to the oxygen atom (a triplet at 3.22 ppm) and methylene (a multiplet at 2.38 ppm) and methyl (a singlet at 2.02 ppm) groups linked to the nitrogen atom were present. The yield of **4** depends both on the reaction time and on the presence of water in the reaction mixture. In a preliminary experiment, the reaction appeared as sluggish and was left for a 24 h at room temperature to afford a 12% crude yield of **4**. When using anhydrous $Na_2SO_4$, the yield increased from 12 to 32%. Presence of the tertiary amino groups with electron-donating methyl substituents increases the basicity of the compound. Moreover, as the mobility of the nitrogen atom is not constrained by inclusion in a ring, compound **4** is more easily hydrolyzed by water and air moisture than the cyclic compound **3**. In compound **4**, hydrolysis of the alkoxyantimony bonds by intramolecular catalysis by the basic nitrogen atom explains the poor yields of the product in the reaction performed in absence of sodium sulfate. When the reaction of triphenylantimony with *N,N*-dimethyl-2-aminoethanol and Bu$^t$OOH was made with a 1:1:1 ratio, we expected to obtain either hydroxy-alkoxy-derivative Sb(V) analogous to those described by V.A. Zinov'eva et al. [36] (Ph$_3$Sb(OH)OCH$_2$CH$_2$NH$_2$), or bis[(*N,N*-dimethyl-2-aminoethoxy)triphenyl]antimony oxide. The formation of the latter was thought to be more likely. However, triphenylantimony oxide turned out to be the only antimony containing product, when the reaction was carried out for 24 h. When reducing the reaction time to 2 h and using anhydrous sodium sulfate, the mixture of compound **4** with Ph$_3$SbO was obtained, as confirmed by IR and $^1$H NMR spectroscopy and HPLC analysis.

$$SbPh_3 + HOCH_2CH_2NMe_2 \xrightarrow[-Bu^tOH,H_2O]{rt,Bu^tOOH}$$

$$Ph_3Sb(OCH_2CH_2NMe_2)_2 \xrightarrow[-2HOCH_2CH_2NMe_2]{H_2O} Ph_3SbO$$

$$(12)$$

Therefore compound **4** formed very rapidly. Then it is hydrolyzed by reason of the high basicity of tertiary amino groups.

## 3. Conclusion

The one-step oxidative reaction of triphenylantimony with OH-containing acidic reagents in the presence of *tert*-butylhydroperoxide can be conveniently extended to silanols as well as to monoalcohols, even in the presence of a neighbouring amino group or to long chain glycols. In contrast to previous attempts [2] that failed to produce the disilyloxy derivatives of triphenylantimony, the present method

offers a mild way of synthesis of these compounds that appear to be rather stable to thermolysis conditions. With long chain glycols, the cyclic compound was formed exclusively instead of the polymer that might have been expected.

## 4. Experimental

### 4.1. General remarks

IR spectra were recorded on a Specord 75IR spectrophotometer in the 4000 –400 cm$^{-1}$ range, for suspension in Nujol or thin film between two optical KBr caps. NMR spectra were measured with a Bruker Avance DPX-200 spectrometer (200 MHz for $^1$H, 50 MHz for $^{13}$C, 39.7 MHz for $^{29}$Si) at 25°C using CDCl$_3$ as solvent and Me$_4$Si as internal standard. Aminoalcohols and trimethylsilanol were analysed on a Tsvet-530 gas chromatograph with a $0.3 \times 200$ cm stainless-steel column (5% SE-30 on Chromaton N-AW-DMCS). HPLC analyses were carried out on a microcolumn liquid chromatograph Milichrom-1A equipped with a $64 \times 2$ mm column, packed with Separon-SGX, Silasorb nitrile with a 5 μm particle diameter, and UV detector. To analyse compound **3**, eluent (hexane: THF 1:1) was used with detection at $\lambda = 230$ nm, and for compound **4** eluent (hexane: THF 10:1) was used with detection at $\lambda = 220$ nm, the eluent velocity being 200 μl/min. The molecular mass of compound **3** was determined by the Rast method [37]. THF, toluene and hexane were distilled from appropriate drying agents. Diethanolamine and *N,N*-dimethyl-2-aminoethanol were purchased (Kaprolaktam Joint-Stock Company, Dzerzhinsk, Russia) and distilled under reduced pressure. *tert*-Butylhydroperoxide [38], triphenylantimony [39], trimethylsilanol and triphenylsilanol [40] were synthesized by known methods. Hexaphenyldisiloxane was prepared by reaction of triphenylsilanol with di-*n*-butylamine [41], m.p. 221°C, lit. 222–224 °C; $^{29}$Si NMR, $\delta$: $-18.5$; $^{13}$C NMR, $\delta$: 127.8, 129.8, 135.2, 135.5.

### 4.2. Synthesis of bis(trimethylsiloxy)triphenylantimony (1)

To a suspension of Na$_2$SO$_4$ (0.50 g) in solution of triphenylantimony (1.50 g, 4.25 mmol) and trimethylsilanol (0.77 g, 8.54 mmol) in toluene (30 ml) a solution of Bu$^t$OOH (0.39 g, 4.38 mmol) in toluene (20 ml) was added dropwise at 0–5 °C. The reaction mixture was stirred over 2 h. Then, the reaction mixture was filtered; the solvent and the volatile products were distilled under reduced pressure. The remaining white solid was recrystallized from hexane to afford compound **1** (1.12 g, 50%) as colourless, transparent crystals. Anal. Calc. for C$_{24}$H$_{33}$O$_2$SbSi$_2$: C, 54.24; H, 6.26; Sb, 22.91; Si, 10.57. Found: C, 53.90; H, 6.34; Sb, 23.57; Si, 11.08%. IR, (cm$^{-1}$): $\nu$ 940 (Sb–O–Si), 1250, 800 (Si–Me), 3060, 1590, 1430, 1070, 740, 695, 455 (Sb–Ph). $^1$H NMR: $\delta$ $-0.02$ (s, 18H, CH$_3$Si); 7.60, 8.27 (both m, 15H, Ph–Sb). $^{13}$C NMR: $\delta$ 3.07 (CH$_3$–Si), 128.9, 130.9, 134.8, 140.4 (Ph–Sb). $^{29}$Si NMR: $\delta$ 2.4. Slow

recrystallization from hexane afforded of a monoclinic form that was used for X-ray crystal structure determination.

### 4.2.1. X-ray crystal structure determination of compound 1

The data were collected on a SMART APEX diffractometer (graphite-monochromated, Mo Kα-radiation, φ–ω-scan technique, $\lambda = 0.71073 E$). The structure was solved by direct methods and was refined on $F^2$ using all reflections with SHELXTL [42] package. SADABS [43] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found from Fourier synthesis and isotropically refined. The details of crystallographic collection and refinement data are given in Table 3. Selected bond lengths and bond angles are given in Table 1.

### 4.2.2. Thermal decomposition of compound 1

0.87 g of compound **1** was heated in a vacuum-sealed two-arm ampule for 1 h at 250 °C. The volatile products (0.03 g of a transparent liquid) were condensed in the side arm. According to GLC analysis and IR spectroscopy, it was identified as hexamethyldisiloxane, obtained in a 13% yield. The residue is a mixture of the initial product and triphenylantimony oxide, as confirmed by IR spectroscopy.

### 4.3. Synthesis of bis(triphenylsiloxy)triphenylantimony (2)

To a suspension of $Na_2SO_4$ (0.50 g) in solution of triphenylantimony (1.50 g, 4.25 mmol) and triphenylsilanol (2.35 g, 8.49 mmol) in toluene (30 ml) a solution of $Bu^tOOH$ (0.39 g, 4.38 mmol) in toluene (20 ml) was added dropwise at 0–5 °C. After the end of the addition of

$Bu^tOOH$, the solution became turbid. The reaction mixture was stirred over 2 h. When the temperature of the mixture reached room temperature, a white precipitate appeared. The solution was decanted; the precipitate was stirred for 2 h in 20 ml of distilled water, filtered, washed with toluene, acetone and air-dried to give **2** (3.20 g, 83%). Compound is partly soluble in $CHCl_3$ and THF and insoluble in $CCl_4$ and acetone. Anal. Calc. for $C_{54}H_{45}O_2SbSi_2$: C,71.76; H, 5.02; Sb, 13.47; Si, 6.21. Found: C, 71.60; H, 4.84; Sb, 13.39; Si, 6.25%. IR (cm$^{-1}$): $v$ 980 (Si–O–Sb), 3060, 1595, 1110, 740, 695, 520, 455 (Si–Ph, Sb–Ph). $^{29}Si$ NMR: $\delta$ −23.9.

### 4.4. Synthesis of 5,5,5-triphenyl-4,6-dioxa-5-stibaperhydroazocine (3)

A solution of diethanolamine (0.24 g, 2.27 mmol) in THF (5 ml) was added to a solution of triphenylantimony (0.80 g, 2.27 mmol) in toluene (20 ml). Then, a solution of $Bu^tOOH$ (0.21 g, 3.34 mmol) in toluene (20 ml) was added dropwise over 1 h. The solution became turbid. The reaction mixture was kept at room temperature for 24 h. The white precipitate was filtered, washed in toluene and air-dried to afford **3** (1.20 g, 62%), m.p. 174 °C. IR (cm$^{-1}$): $v$ 3150, 1540 (N–H), 2820, 2775, 2725, (N–CH$_3$), 1050 (Sb–O–C), 3060, 1580, 1430, 1070, 740, 700, 455 (Sb-Ph). $^1H$ NMR: $\delta$ 2.76 (2H; NCH$_2$), 2.97 (m, 1H; NH), 3.19 (m, 2H; NCH$_2$), 4.05 (m, 4H; OCH$_2$), 7.32–7.76 (m, 15H; Sb-Ph). M (RAST method) 478, calc. 456. Anal. Calc for $C_{22}H_{24}O_2NSb$: C, 57.92; H, 5.30; Sb, 26.69. Found: C, 58.04; H, 5.28; Sb, 26.00%.

### 4.5. Reaction of triphenylantimony with 2-(N,N-dimethylamino)-ethanol in the presence of Bu$^t$OOH in the ratio of 1:2:1

(a) A solution of $Bu^tOOH$ (0.32 g, 3.51 mmol) in toluene (15 ml) was added dropwise to a stirred solution of triphenylantimony (1.20 g, 3.40 mmol) and 2-(N,N-dimethylamino)ethanol (0.61 g, 6.85 mmol) in toluene (30 ml). The mixture was stirred for 2 h and then left at room temperature for 24 h. Removal of the volatiles under reduced pressure gave a white viscous residue, that was extracted with hot hexane (3 × 10 ml) to afford 0.26 g of a transparent viscous liquid, as a mixture of bis[2-(N,N-dimethylamino)ethoxy]triphenylantimony (**4**) and triphenylantimony oxide (∼20% mol). The yield of compound **4** was 12%. IR (cm$^{-1}$): $v$ 2820, 2775, 2725 (N–CH$_3$), 2980, 2945, 2860, 1460 (C-H), 1050 (Sb–O–C), 3060, 1605, 1580, 1480, 1430, 1070, 830, 700, 455 (Sb–Ph). $^1H$ NMR: $\delta$ 2.02 (C; 12H; N(CH$_3$)$_2$), 2.38 (m, 4H; NCH$_2$), 3.22 (t, 4H; OCH$_2$), 7.32–7.76 (m, 15H; Sb-Ph).

(b) To the suspension of $Na_2SO_4$(1.2 g) in a solution of triphenylantimony (1.20 g, 3.40 mmol) and N,N-dimethyl-2-aminoethanol (0.61 g, 6.85 mmol) in toluene (30 ml) a solution of $Bu^tOOH$ (0.32 g, 3.51 mmol)

Table 3
Details of crystallographic collection and refinement data for **1**

| | |
|---|---|
| Empirical formula | $C_{24}H_{33}O_2SbSi_2$ |
| Molecular weight | 531.43 |
| Crystal system | Monoclinic |
| Temperature (K) | 100(2) |
| Space group | $P2(1)/n$ |
| Unit cell dimensions | |
| $a$ (E) | 8.7426(5) |
| $b$ (E) | 27.7083(15) |
| $c$ (E) | 10.6657(6) |
| $\beta(°)$ | 101.9060(10) |
| $V$ ($E^3$) | 2528.1(2) |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 1.396 |
| Absorption coefficient (mm$^{-1}$) | 1.203 |
| $F(000)$ | 1088 |
| Crystal size (mm$^3$) | 0.08 × 0.08 × 0.08 |
| $2\theta_{max}$ (°) | 58 |
| Reflections collected | 26598 |
| Independent reflections | 6705 [$R_{int} = 0.0264$] |
| Absorption correction | SADABS |
| Data/ restraints/ parameters | 6705/ 0/ 394 |
| Goodness-of-fit on $F^2$ | 1.303 |
| $R_1/wR_2$ ($I > 2\sigma(I)$) | 0.0396/0.0802 |
| $R_1/wR_2$ (all data) | 0.0431/0.0815 |
| Largest diffraction peak and hole (e E$^{-3}$) | −0.874/1.036 |

in toluene (15 ml) was added dropwise over 2 h. The reaction was stirred for 24 h. After the solvent and the easily-volatile products were removed, hexane extraction of the residue gave 0.73 g of compound **4** isolated as a mixture with triphenylantimony oxide ($\sim$20% mol). The yield of compound **4** is 32%.

### 4.6. The reaction of triphenylstibium with 2-(N,N-dimethylamino)-ethanol in the presence of Bu$^t$OOH in the ratio of 1:1:1

(a) The solution of 0.32 g (3.51 mmol) of Bu$^t$OOH in 15 ml of toluene was added dropwise over 1 h under stirring to the solution of 1.20 g (3.40 mmol) of triphenylstibin and 0.30 g (3.36 mmol) of 2-(N,N-dimethylamino)-ethanol in 30 ml of toluene. The mixture left at room temperature for 24 h. After the solvent and volatile products had been distilled under reduced pressure, 1.40 g of (Ph$_3$SbO)$_n$ was isolated as a white powder. IR, cm$^{-1}$: 3060, 1605, 1580, 1480, 1430, 1070, 830, 700, 455 (Sb–Ph), 670, 650 (Sb–O).

(b) To the suspension of 1.20 g Na$_2$SO$_4$ in the solution of 1.20 g (3.40 mmol) of triphenylstibin and 0.30 g (3.36 mmol) of 2-(N,N-dimethylamino)-ethanol in 30 ml toluene the solution of 0.32 g (3.51 mmol) of Bu$^t$OOH in 15 ml toluene was added dropwise over 2 h under stirring. After the solvent and the easily-volatile products were removed, hexane extraction of the residue gave 0.19 g of compound **4** was isolated as a mixture with triphenylantimony oxide ($\sim$20% mol). The yield of compound **4** is 8%. IR, cm$^{-1}$: 2820, 2775, 2725 (N–CH$_3$), 2980, 2945, 2860, 1460 (C–H), 1050 (Sb–O–C), 3060, 1605, 1580, 1480, 1430, 1070, 830, 700, 455 (Sb–Ph). $^1$H NMR, $\delta$: 2.02 (C; 12H; N(CH$_3$)$_2$), 2.38 (m, 4H; NCH$_2$), 3.22 (t, 4H; OCH$_2$), 7.32–7.76 (m, 15H; Sb–Ph).

### Acknowledgement

### Appendix A. Supplementary material

CCDC 264895 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.019.

### References

[1] T.C. Thepe, R.J. Garascia, M.A. Selvoski, A.N. Patel, Ohio J. Sci. 77 (1977) 134–135.
[2] V.A. Dodonov, T.I. Zinov'eva, Organomet. Chem. USSR 5 (1992) 1265–1271.
[3] V.A. Dodonov, A.V. Gushchin, O.G. Vorob'ev, T.I. Zinov'eva, Russ. Chem. Bull. 43 (1994) 497–498.
[4] D.V. Moiseev, A.V. Gushchin, A.S. Shavirin, Yu.A. Kursky, V.A. Dodonov, J. Organomet. Chem. 667 (2003) 176–580.
[5] V.V. Sharutin, I.V. Egorova, I.I. Pavlushkina, A.P. Pakusina, N.V. Nasonova, M.A. Pushilin, A.V. Gerasimenko, E.A. Gerasimenko, A.S. Sergienko, Russ. J. Coord. Chem. 29 (2003) 83–88.
[6] V.A. Dodonov, S.N. Zaburdyaeva, N.N. Nevkina, Organomet. Chem. USSR 2 (1989) 1296–1297.
[7] V.A. Dodonov, A.Y. Fedorov, R.I. Usyatinsky, S.N. Zaburdyaeva, A.V. Gushchin, Russ. Chem. Bull. 44 (1995) 730–733.
[8] S.N. Zaburdyaeva, L.S. Korchemnaya, A.Y. Fedorov, V.A. Dodonov, Russ. J. Gen. Chem. 69 (1999) 86–88.
[9] V.A. Dodonov, A.V. Gushchin, D.A. Gor'kaev, G.K. Fukin, T.I. Starostina, L.N. Zakharov, Y.A. Kurskii, A.S. Shavyrin, Russ. Chem. Bull. 51 (2002) 1051–1057.
[10] V.V. Sharutin, O.K. Sharutina, O.V. Molokova, A.P. Pakusina, E.N. Bondar', D.B. Krivolapov, A.T. Gubaidullin, I.A. Litvinov, Russ. J. Gen. Chem. 71 (2001) 1426–1430.
[11] A.V. Gushchin, V.A. Dodonov, R.I. Usyatinsky, E.R. Koreshkova, B.B. Tipanov, Russ. Chem. Bull. 43 (1994) 1239–1241.
[12] A.G. Davies, S.C.W. Hook, J. Chem. Soc. (C) (1971) 1660.
[13] H. Schmidbaur, H.S. Arnold, E. Beinhofer, Chem. Ber. 97 (1964) 449–458.
[14] G.A. Razuvaev, T.G. Brilkina, E.V. Krasilnikova, T.I. Zinov'eva, A.I. Filimonov, J. Organomet. Chem. 40 (1972) 151–157.
[15] J. Homer, A.W. Jarvie, J. Hickton, J. Chem. Soc. B (1967) 67–71.
[16] G. Engelhardt, M. Magi, E. Lippmaa, J. Organomet. Chem. 54 (1973) 115–122.
[17] I.T. Goronovskii, Yu.P. Nazarenko, E.F. Nekryach, The Short Reference Book on the Chemistry, Naukova Dumka, Kiev, 1987.
[18] V.A. Lebedev, R.I. Bochkova, L.F. Kuzubova, E.A. Kuz'min, V.V. Sharutin, N.V. Belov, Dokl. Chem. 265 (1982) 332–335.
[19] V.V. Sharutin, O.K. Sharutina, L.P. Panova, N.V. Nasonova, T.N. Bliznyuk, V.K. Belsky, Russ. Chem. Bull. 48 (1999) 173–175.
[20] R. Ruther, F. Huber, H. Preut, Z. Anorg. Allg. Chem. 539 (1986) 110–126.
[21] G. Ferguson, C. Glidewell, D. Lloyd, S. Metcalfe, J. Chem. Soc., Perkin Trans. 2 (1988) 731–735.
[22] H. Barucki, S.J. Coles, J.F. Costello, T. Gelbrich, M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (2000) 2319–2325.
[23] G. Ferguson, B. Kaitner, C. Glidewell, S. Smith, J. Organomet. Chem. 419 (1991) 283–291.
[24] M. Baier, P. Bissinger, H. Schmidbaur, Organometallics 12 (1993) 2208–2212.
[25] M. Baier, K. Angermaier, H. Schmidbaur, Z. Naturforsch B: Chem. Sci. 49 (1994) 855–858.
[26] K.-W. Shen, W.E. McEwen, S.J. La Placa, W.C. Hamilton, A.P. Wolf, J. Am. Chem. Soc. 90 (1968) 1718–1723.
[27] S. Pankaj, N. Rosas, G. Espinosa-Perez, A. Cabrera, Acta Cryst., Section C 52 (1996) 889–891.
[28] A. Gupta, R.K. Sharma, R. Bohra, V.K. Jain, J.E. Drake, M.B. Hursthouse, M.E. Light, Polyhedron 21 (2002) 2387–2392.
[29] D.B. Sowerby, J. Chem. Res. (S) (1979) 80.
[30] M. Domagala, F. Huber, H. Preut, Z. Anorg. Allg. Chem. 574 (1989) 130–142.
[31] M. Domagala, F. Huber, H. Preut, Z. Anorg. Allg. Chem. 582 (1990) 37–50.
[32] M.L. Glowka, D. Martynowski, K. Kozlowska, J. Mol. Struct. 474 (1999) 81–89.

[33] R. Nomura, M. Kori, H. Matsuda, Chem. Lett. 5 (1985) 579–580.
[34] D. Kraft, M. Wieber, Z. Anorg. Allg. Chem. 605 (1991) 137–143.
[35] P. Hegyes, S. Foldeak, P. Hencsei, G. Zsombok, J. Nagy, J. Organomet. Chem. 251 (1983) 289–294.
[36] V.A. Zinov'eva, I.V. Shalygina, VI All-Russian Conference on Organometallic Chemistry (Nizhnii Novgorod 22-25 September 1995), Nizhnii Novgorod 1995, Abstr., 1, 165.
[37] A.N. Nesmejanov, N.A. Nesmejanov, Bases of the Organic Chemistry, V.1, Khimiya, Moskow, 1974.
[38] V. Karnojitzki, Les Peroxydes Organiques, Hermann, Paris, 1964.

[39] T.V. Talalaeva, K.A. Kocheshkov, Zh. Obshch. Khim. 16 (1946) 777.
[40] M.B. Shostakovskii, I.A. Shihiev, D.A. Kochkin, V.I. Belaev, J. Gen. Chem. USSR 24 (1954) 2202–2206.
[41] H. Gilman, B. Hofferth, H.W. Melvin, G.E. Dunn, J. Am. Chem. Soc. 72 (1950) 5767–5768.
[42] G.M. Sheldrick, SHELXTL v. 6.12, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 2000.
[43] G.M. Sheldrick, SADABS v.2.01, Bruker/Siemens Area Detector Absorption Correction Program, Bruker AXS, Madison, Wisconsin, USA, 1998.