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Reviews

Low-Valent Organoantimony and -bismuth Compounds with Neopentyl and (Trimethylsilyl)methyl Substituents

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Recent developments in the field of organometallic compounds of antimony or bismuth in the oxidation states ≤I or II with $(Me_3Si)_2CH$, Me_3SiCH_2, and Me_3CCH_2 as substituents are described in this review. These alkyl compounds are useful for comparative studies aiming at the recognition of specific features in the chemistry of low-valent compounds of the heavy pnicogens. Characteristic differences emerge when reactions of the ring systems $(RE)_n$ (R = Me_3SiCH_2; E = Sb, $n = 4, 5$; E = Bi, $n = 3, 5$) with $W(CO)_5$(tetrahydrofuran) are considered. Under similar conditions the antimony rings react with coordination of the intact five-membered homocycle, whereas the bismuth rings are transformed into a dibismuthene ligand.

Introduction

Recent years have witnessed considerable progress in the field of low-valent organometallic compounds of antimony or bismuth in the oxidation states ≤I or II, where structures with Sb−Sb or Bi−Bi bonds prevail. Highlights are distibenes and dibismuthenes, *trans*-RE═ER (E = Sb, Bi), protected by bulky aryl groups R,[1−3] and antimony and bismuth monocycles $(RE)_n$ (E = Sb, $n = 3-6$; E = Bi, $n = 3-5$)[4,5] or polycycles R_4Sb_8[5] and R_6Bi_8.[6] Stibinidenes, RSb, or distibenes were stabilized as ligands in the coordination spheres of transition-metal carbonyl complexes.[7,8]

Many low-valent organoantimony or -bismuth compounds are sensitive molecules with rather weak bonds and highly reactive functional groups. Often there is a strong tendency for scrambling reactions, which makes it difficult to follow rational designs of synthetic pathways. The problem of instability can usually be overcome by steric protection. However, the protecting groups have a strong influence on the chemical behavior of the protected species and some very bulky substituents reduce the reactivity or have a leveling effect that makes it difficult to recognize specific features: e.g., a possible exceptional stabilization of low-valent bismuth compounds due to relativistic effects.[9] During the past decade it emerged that the alkylantimony or -bismuth compounds bearing $(Me_3Si)_2CH$, Me_3SiCH_2, or Me_3CCH_2 groups are useful for comparative studies, and we present here an overview of recent developments in the synthetic chemistry of low-valent antimony and bismuth compounds bearing these alkyl groups.

Bis((trimethylsilyl)methyl)antimony and -bismuth Compounds

Syntheses and Reactions of R_2ECl, $RECl_2$ (E = Sb, Bi; R = $(Me_3Si)_2CH$). (Bis(trimethylsilyl)methyl)antimony and -bismuth chlorides are valuable starting materials for the synthesis of a wide variety of low-valent compounds of antimony or bismuth. The monochlorides R_2ECl (E = Sb,[10] Bi;[11] R = $(Me_3Si)_2CH$) are synthesized by reactions of RLi with ECl_3. The Grignard reaction of RMgCl with $SbCl_3$ gives $RSbCl_2$.[7,12] This route is only viable with bulky groups such as the bis(trimethylsilyl)methyl group. Addition of HCl to $RBi(C_6H_5)_2$ leads to $RBiCl_2$.[11] All these syntheses were performed with good yields and high purity of the products. Crystal structure analyses revealed that R_2SbCl and R_2BiCl are monomeric.[11,13] $RSbCl_2$ is loosely associated to dimers,[13] whereas the diethyl ether adduct of the bismuth dichloride adopts a polymeric structure, where the $RBiCl_2$ molecules are closely associated through intermolecular Bi···Cl contacts.[11] These structures reflect the more Lewis acidic character of the bismuth centers compared with antimony. An overview

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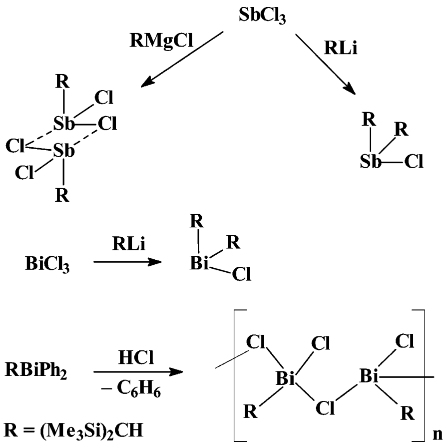
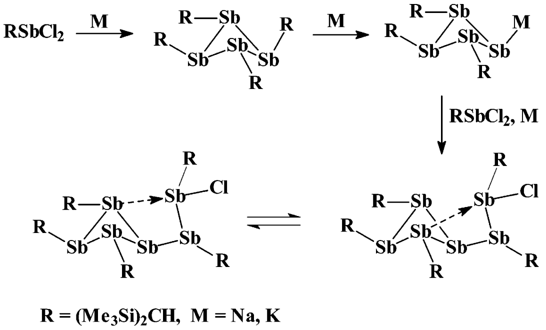
Scheme 1



Scheme 2



of synthetic and some structural aspects of the bis((trimethylsilyl)methyl)antimony and bismuth chlorides is presented in Scheme 1.

The elimination of chlorine from the bis((trimethylsilyl)methyl)antimony chlorides is achieved by reactions with Mg in tetrahydrofuran (thf) or Li_3Sb in liquid ammonia and the stibines R_4Sb_2,[12] cyclo-R_nSb_n (n = 3, 4) and R_4Sb_8 (R = $(Me_3Si)_2CH$) form.[5] The cyclobismuthines R_4Bi_4 and R_3Bi_3 (R = $(Me_3Si)_2CH$) were first obtained by reacting $RBiCl_2$ with Mg in thf.[5] A recent development is the dehalogenation of $RSbCl_2$ by Na/K alloy with formation of the pentaalkylchlorohexastibine Sb_6R_5Cl (R = $(Me_3Si)_2CH$) in a small (5%) but reproducible yield together with cyclo-R_nSb_n (n = 3, 4).[15] The structure of Sb_6R_5Cl combines the motives of antimony rings and chains. ^1H NMR spectra reveal that two isomers exist in solution. Two probable solution structures and a reaction path are presented in Scheme 2. The formation of Sb_6R_5Cl is probably related to an intramolecular dative interaction between one of the Sb atoms in the ring as donor and a terminal Sb atom of the chain as acceptor.

The structure of Sb_6R_5Cl in the crystal is shown in Figure 1. The four-membered antimony ring is folded; the positions of the substituents on the ring correspond to the all-trans configuration. The value of the Sb····Sb−Cl angle of 166.20(2)° confirms the donor−acceptor model because the acceptor orbital is expected to lie opposite to the Sb−Cl bond.

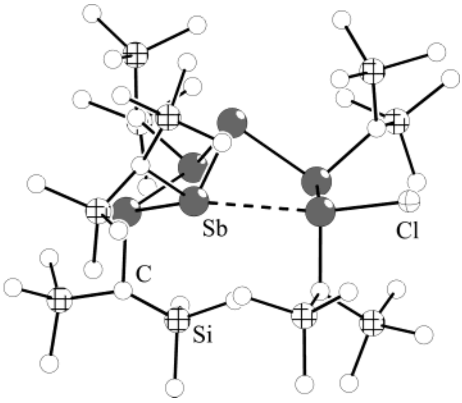


Figure 1. Structure of Sb_6R_5Cl (R = $(Me_3Si)_2CH$) in the crystal state.

Syntheses and Reactions of R_2EH and REH_2 (E = Sb, Bi), R(H)SbSb(H)R, $RSbD_2$, and R(D)Sb−Sb(D)R (R = $(Me_3Si)_2CH$). The synthetic pathways leading to the bis((trimethylsilyl)methyl)antimony and -bismuth hydrides are similar, but the thermal stability differs considerably. Only the stibines are stable enough to allow manipulations at and above room temperature. The bismuthines are synthesized at low temperatures, and they are used in situ for further reactions. Both groups of compounds are excellent starting materials for synthetic purposes.

The monohydrides R_2EH (R = $(Me_3Si)_2CH$) are formed by reactions of R_2ECl with $LiAlH_4$ in 66% (E = Sb) or 73% yield (E = Bi).[16] Solutions of R_2SbH are stable in sealed tubes up to 105 °C. Also, exposure to UV light does not lead to decomposition. Solutions of R_2BiH in benzene or diethyl ether are stable only below −20 °C. The E−H stretching vibrations of the monohydrides are observed at 1840 cm^{-1} (E = Sb) or 1690 cm^{-1} (E = Bi). Reactions of $RECl_2$ with $LiAlH_4$ lead to different products, depending on the conditions. The dihydrides REH_2 (R = $(Me_3Si)_2CH$, E = Sb, Bi) form when the corresponding dichlorides are added to $LiAlH_4$. The reverse procedure, i.e., addition of $LiAlH_4$ to a solution of $RSbCl_2$ in diethyl ether at −78 °C gives the distibine R(H)SbSb(H)R (R = $(Me_3Si)_2CH$) in 93% yield. $RSbH_2$ is stable up to 110 °C.[17] Decomposition of $RBiH_2$ occurs at temperatures above −35 °C.[18] The distibine is a yellow crystalline solid stable at room temperature for a long time. Crystals consist exclusively of *meso*-R(H)SbSb(H)R in the *antiperiplanar* conformation (Figure 2). The values for the Sb−H bond lengths are 170.5(8) and 176(4) pm. They were determined by neutron diffraction.[19]

meso-R(H)Sb−Sb(H)R is not stable in solution. NMR spectra reveal that $RSbH_2$, R(H)SbSbRSb(H)R, and *d*,*l*-R(H)SbSb(H)R form in equilibria (eq 1) when crystals

$$\begin{gathered} 2\ meso\text{-R(H)SbSb(H)R} \rightleftharpoons \text{RSbH}_2 + \\ \text{R(H)SbSbRSb(H)R} \rightleftharpoons 2\ d,l\text{-R(H)SbSb(H)R} \quad (1) \\ \text{R} = (\text{Me}_3\text{Si})_2\text{CH} \end{gathered}$$

of *meso*-R(H)Sb−Sb(H)R are dissolved in C_6D_6.[19] Re-

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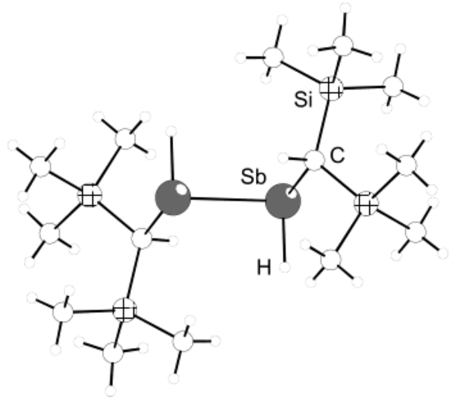
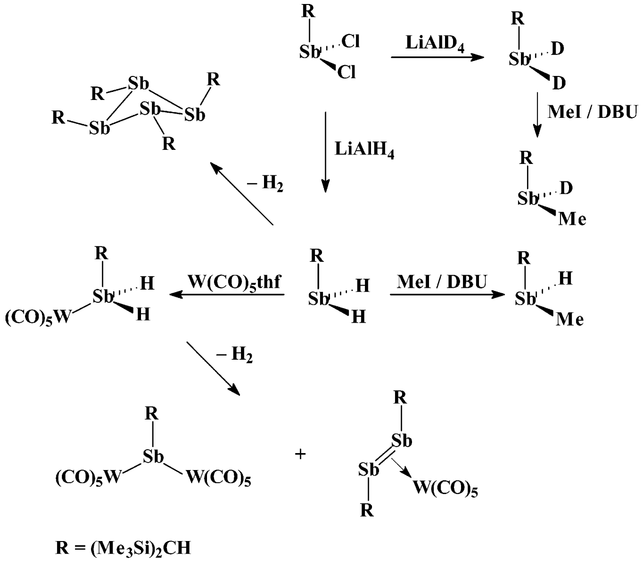


Figure 2. Structure of *meso*-R(H)SbSb(H)R (R = $(Me_3Si)_2CH$) in the crystal state.

Scheme 3



actions between $RSbCl_2$ and $LiAlD_4$ give $RSbD_2$ and R(D)SbSb(D)R.[19]

The thermal stability of $RSbH_2$ (R = $(Me_3Si)_2CH$) is remarkable for a primary stibine. It is stable up to 110−120 °C when the elimination of H_2 occurs and cyclo-R_4Sb_4 is formed. Simple alkylstibines evolve hydrogen even at room temperature. The reaction of $RSbH_2$ with $W(CO)_5$thf at room temperature gives $RH_2SbW(CO)_5$. Elimination of hydrogen from $RH_2SbW(CO)_5$ leads to the blue complex $RSb[W(CO)_5]_2$. This compound was synthesized before by Cowley et al. by reacting $RSbCl_2$ with $[W(CO)_5]^{2-}$.[7] It belongs to the family of "open" stibinidene complexes, where the coordination at the antimony center is planar and bonding interactions between the tungsten atoms can be ruled out. The primary stibine $RSbH_2$ is also useful for the synthesis of secondary stibines with two different alkyl groups where antimony is a center of chirality. One example is R(Me)SbH, a racemic chiral stibine that was obtained by selective substitution of one hydrogen atom in $RSbH_2$ with MeI and diazabicycloundecene (DBU).[19] An overview of the chemistry of $RSbH_2$ and $RSbD_2$ is given in Scheme 3.

The reaction of R(H)SbSb(H)R (R = $(Me_3Si)_2CH$) with $W(CO)_5$thf leads to the distibine complexes *meso*- and *d,l*-R(H)SbSb(H)R$[W(CO)_5]_2$. Selective crystallization results in the separation of the *meso* isomer from the *d,l* forms. *d,l*-R(H)Sb−Sb(H)R$(W(CO)_5)_2$ crystallizes as a 1:1 mixture of the two enantiomers. The distibine complexes react in solution with evolution of hydrogen and $W(CO)_5$ to form *trans*-(RSb═SbR)$W(CO)_5$, a distibene complex with *side-on* coordination of the ligand.[19]

Substitution of the hydrogen atoms in R(H)SbSb(H)R is achieved by reacting the distibine with MeI and DBU. and the isomers *meso*- and *d,l*-R(Me)Sb−Sb(Me)R are obtained.[19]

R(H)SbSb(H)R is also a valuable source for the syntheses of various antimony homocycles. Addition of $LiAlH_4$ to the distibine gives cyclo-R_3Sb_3 and cyclo-R_4Sb_4 in the cis,trans configuration, which is very unusual for four-membered pnicogen rings. A probable precursor molecule of the four-membered ring is the distibene RSb═SbR. When *cis,trans*-R_4Sb_4 is exposed to sunlight, in the first step isomerization to the more stable isomer *all-trans*-R_4Sb_4 takes place and in the second step the photochemical ring contraction with formation of cyclo-R_3Sb_3 occurs. A bicyclic stibine, R_6Sb_8, was obtained in low yield in an attempt to metalate R(H)SbSb(H)R with tBuONa. The tricyclic stibine R_4Sb_8 is formed in 32% yield when R(H)SbSb(H)R is reacted with $SbCl_3$ in the presence of pyridine. Both R_6Sb_8 and R_4Sb_8 decompose photochemically with formation of cyclo-R_3Sb_3. An overview of the chemistry of R(H)SbSb(H)R is given in Scheme 4.

Coordination Chemistry of cyclo-R_3Sb_3 (R = $(Me_3Si)_2CH$). Already the first studies of reactions of the tristibirane cyclo-R_3Sb_3 (R = $(Me_3Si)_2CH$) with transition-metal carbonyl complexes have revealed a manifold coordination chemistry of this antimony ring, which can coordinate as an intact ligand or react with insertion into one or all of the Sb−Sb bonds. Known reactions of cyclo-R_3Sb_3 are presented in Scheme 5.

The reaction of the tristibirane with $Fe_2(CO)_9$ leads to an insertion of an $Fe(CO)_4$ unit into the bond between the antimony atoms bearing alkyl groups in cis positions and formation of $R_3Sb_3Fe(CO)_4$,[20] a heterocyclic complex which is isolobal with the homocycle R_4Sb_4. Between the hetero- and the homocycle there are close structural relations. Both rings are folded, and the substituents adopt a maximum number of trans positions. When the tristibirane is reacted with $Mn(CO)_2C_5H_4CH_3$thf, a complete degradation of the antimony ring system results and the blue compound $RSb[Mn(CO)_2C_5H_4CH_3]_2$, a novel example of an "open" stibinidene complex, is formed. Also, the reaction of R_3Sb_3 with $Co_2(CO)_8$ results in ring degradation. The product is $[(RSb)_2Co_2(CO)_6]$, a bis(stibinidene) complex with two RSb units in bridging positions between two cobalt centers.[21] The distance between the Sb atoms (306.9(6) pm) is longer than average Sb−Sb single-bond lengths (285 pm) but considerably shorter than the sum of van der Waals radii of two Sb atoms (440 pm). These values indicate the presence of weak bonding interactions between the antimony centers. Coordination of the intact tristibirane is achieved in the reaction with $W(CO)_5$thf, which leads to the formation of $R_3Sb_3[W(CO)_5]$.[21] The tungsten atom is coordinated to one of the Sb atoms bearing a R group

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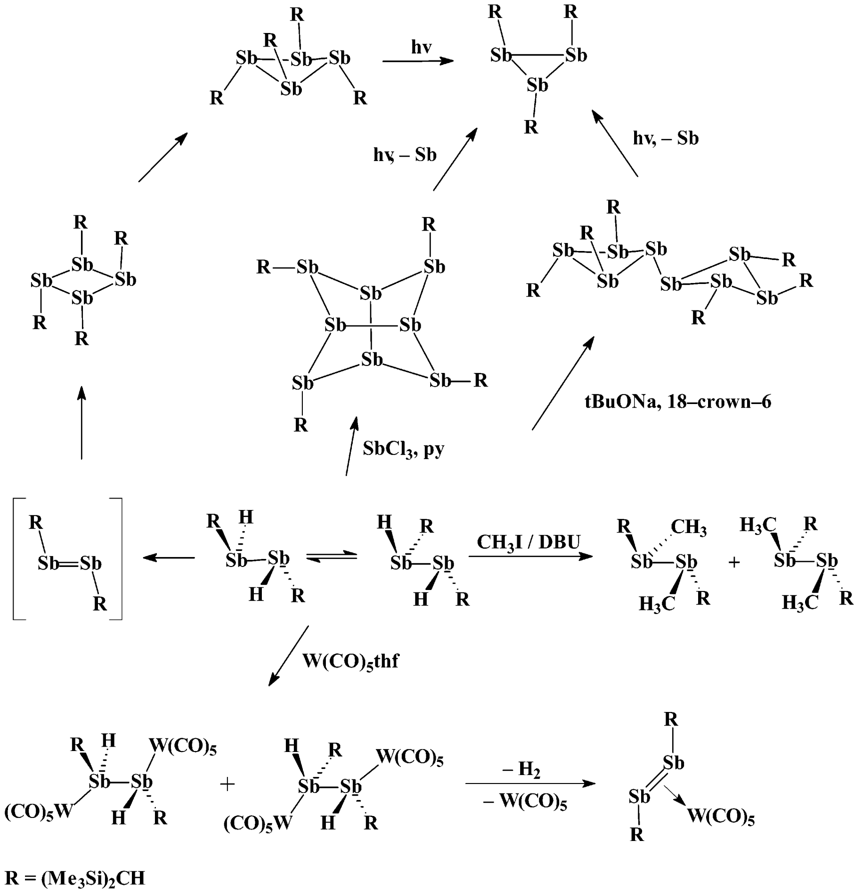
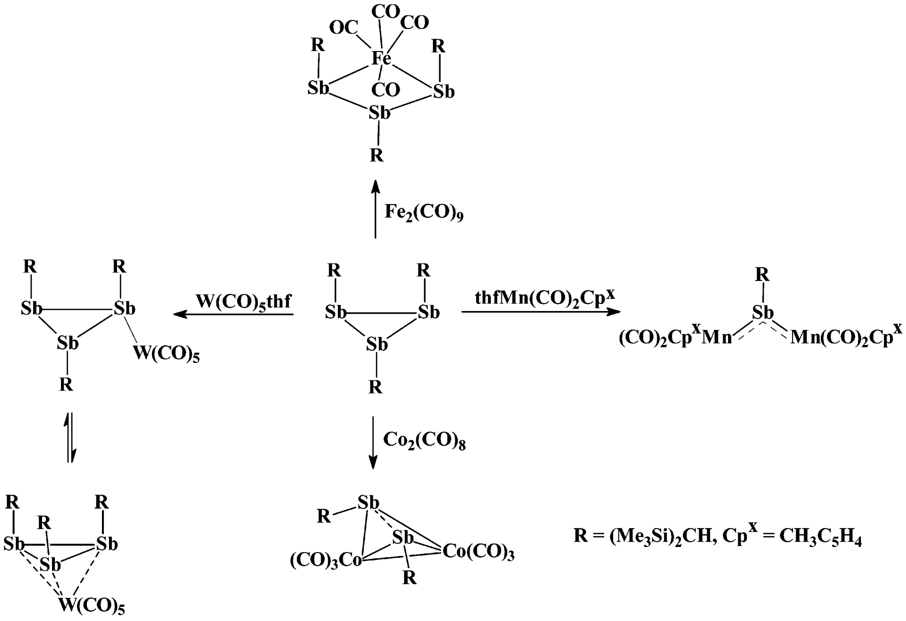
Scheme 4



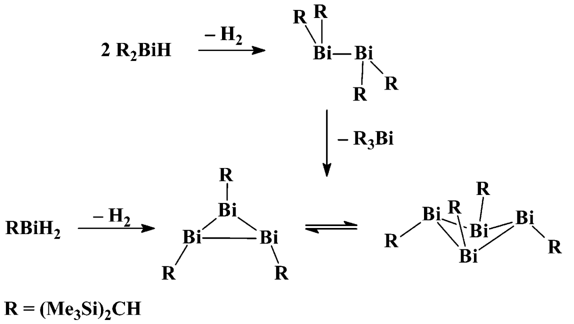
Scheme 5



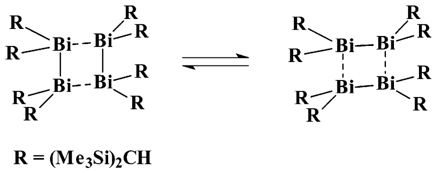
with cis–trans relations to neighboring substituents. This coordination pattern is not only observed in the crystalline state but also in solution at room temperature, where the NMR spectra reflect the nonequivalence of the R groups. The observed coalescence of the signals above 40 °C can be rationalized by assuming W(CO)$_5$ migration and antimony inversion as rapid processes on the NMR time scale.

Reactions of R$_2$BiH and RBiH$_2$ (R = (Me$_3$Si)$_2$CH) with Formation of a Dibismuthine and Cyclobismuthines. A convenient method for the formation of organometallic compounds with bismuth–bismuth bonds is the thermal decomposition of primary or secondary bismuthines. The decomposition of R$_2$BiH (R = (Me$_3$Si)$_2$CH) with formation of H$_2$ and R$_2$BiBiR$_2$ proceeds at room temperature.[16] The cycles R$_n$Bi$_n$ (n = 3,

Scheme 6



Scheme 7

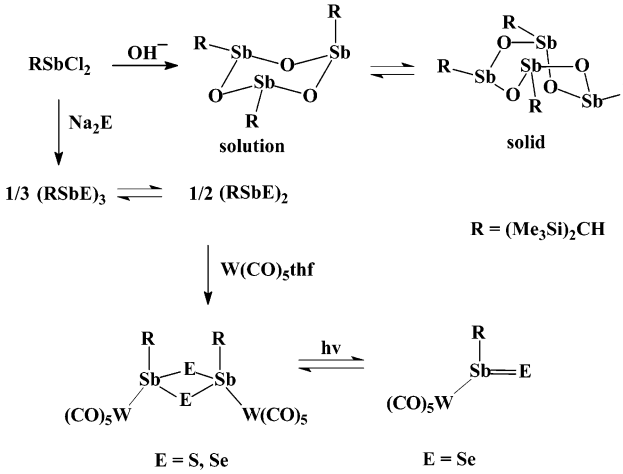


4; R = $(Me_3Si)_2CH$) are obtained by elimination of R_3Bi from the dibismuthine or by decomposition of $RBiH_2$ at −35 °C.[18] They form a ring system consisting of *all-trans*-R_4Bi_4 in the solid phase and the trimer−tetramer equilibrium with *cis,trans*-R_3Bi_3 in benzene solution.[22] Pathways describing the decomposition reactions are depicted in Scheme 6.

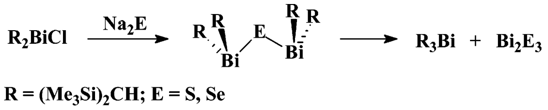
The dibismuthine R_4Bi_2 exhibits an interesting dynamic behavior that was investigated by temperature-dependent NMR spectroscopy in benzene or toluene solutions of varying concentrations. Monomeric dibismuthine molecules were observed only at high dilution ($c = 6.97 \times 10^{-7}$ mol L^{-1}) at room temperature. At higher concentrations and lower temperatures there are weakly associated dimers or equilibria reactions leading to an intermolecular exchange of the R_2Bi groups (Scheme 7). Dissociation of the central Bi−Bi bond with formation of $R_2Bi^{\bullet}$ radicals was, however, not observed.[16]

Antimony heterocycles $(RSbE)_n$ (R = $(Me_3Si)_2CH$; E = O, S, Se, Te; $n = 2-4$). The bis(trimethylsilyl)methyl group is not only efficient for the stabilization of homocycles but also suitable to protect the heterocycles $(RSbE)_n$ (R = $(Me_3Si)_2CH$; E = O, S, Se, Te; $n = 2-4$).[13,23] The first synthetic and structural studies and also the results of a single-crystal structure analysis of the tetramer cyclo-$(RSbO)_4$ as an *all-trans* isomer in the boat conformation were reported several years ago.[23] ^1H NMR studies revealed, however, that solutions contain mainly cyclo dimers and trimers. A recent result is the trapping of the heterocyclic dimers $(RSbE)_2$ (E = S, Se) in cyclo-$(RSbE)_2[W(CO)_5]_2$.[24,25] These complexes contain dative bonds from the antimony atoms to the tungsten centers. The alkyl groups are in cis positions relative to each other. The tungsten pentacarbonyl moieties are bonded trans to the alkyl groups. Solutions of (*cis*-$RSbSe)_2[W(CO)_5]_2$ in C_6D_6 are photosensitive. Irradiation leads to a species with equivalent R groups: probably the monomeric complex $RSbSeW(CO)_5$. An overview of the reactivity of the (bis(trimethylsilyl)methyl)antimony chalcogenides is given in Scheme 8. Analogous bismuth compounds are not known.

Scheme 8



Scheme 9



Bis(dialkylbismuth) Chalcogenides, $(R_2Bi)_2E$ (E = S, Te; R = $(Me_3Si)_2CH$). The dibismuth chalcogenides $(R_2Bi)_2E$ (E = S, Te; R = $(Me_3Si)_2CH$) are formed in 88% (E = S) or 53% (E = Te) yield from R_2BiCl with Na_2S in water or with Na_2Te in liquid ammonia.[24] Both compounds are unstable at room temperature. They decompose with formation of R_3Bi and bismuth chalcogenides (Scheme 9). In the crystal the molecules adopt near syn,syn conformations, where the dihedral angles between the assumed direction of the lone pair of electrons at Bi and the Bi−E bonds lie between 20 and 63°. $R_2BiTeBiR_2$ is the first molecule with a Bi−Te bond that was characterized by X-ray diffraction. The Bi−Te bond lengths are 287.2(3) and 288.9(2) pm.

Neopentyl and Trimethylsilyl Antimony and Bismuth Compounds

Syntheses and Structures of Neopentyl and Trimethylsilyl Antimony and Bismuth Rings. Me_3CCH_2 and Me_3SiCH_2 groups are also effective protecting groups for cyclostibines and cyclobismuthines or coordination compounds derived from these ligands. The chemistry of these compounds differs considerably from that of the analogous bis(trimethylsilyl)methyl derivatives, thus reflecting the more relaxed steric situation, which leads to a higher reactivity. Valuable starting materials are the dihalides $Me_3CCH_2SbBr_2$,[26] $Me_3SiCH_2SbCl_2$,[27] $Me_3CCH_2BiCl_2$,[28] and Me_3SiCH_2-

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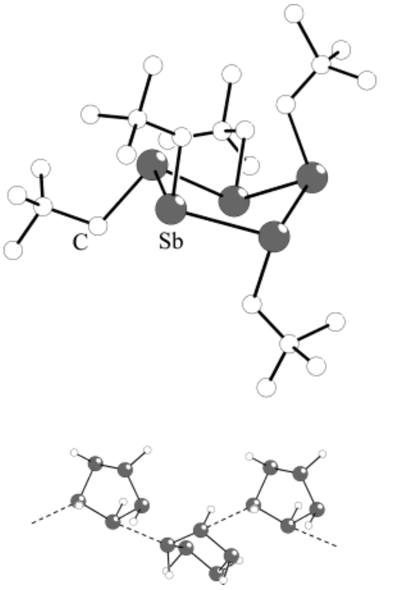
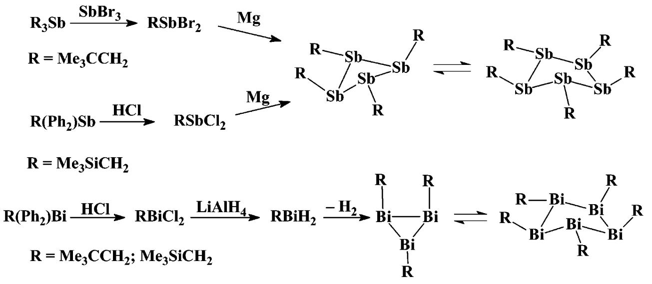


Figure 3. Molecular structure of $(Me_3CCH_2Sb)_5$ (above) and arrangement of the molecules in the crystal state.

Scheme 10



$BiCl_2$.[29] Sb homocycles are formed from the dihalides by reduction with Mg in thf. The homocycles of bismuth are obtained by elimination of hydrogen from the corresponding hydrides at low temperatures. Synthetic pathways are summarized in Scheme 10.

The inspection of analogous Sb and Bi ring systems reveals characteristic differences. The neopentyl- and ((trimethylsilyl)methyl)antimony rings exist in solution as an equilibrium mixture of tetramers and pentamers, with the latter being much more abundant even at high dilution. In contrast, in the bismuth ring systems trimers and pentamers are the most abundant species. This remarkable preference for odd-membered rings may result from stabilizing cis−cis (lone pair−lone pair) interactions. X-ray structure analyses on $(RE)_n$ ($R = Me_3CCH_2$, E = Sb, Bi; $R = Me_3SiCH_2$, E = Sb) revealed that crystalline phases consist of pentamers.[28] Crystals of $(Me_3CCH_2Sb)_5$ contain Sb_5 rings in a near-envelope conformation with the substituents in a maximum of trans positions. The molecular structure of $(Me_3CCH_2Sb)_5$ is depicted in Figure 3. The pentastibolane rings are weakly associated to chains through intermolecular contacts between antimony atoms. ^1H NMR spectra of $(Me_3CCH_2Sb)_5$ in C_6D_6 at room temperature contain three singlet signals in a 2:2:1 intensity ratio for the CH_3 groups as well as a singlet and eight signals of two AB spin systems for the CH_2 groups.

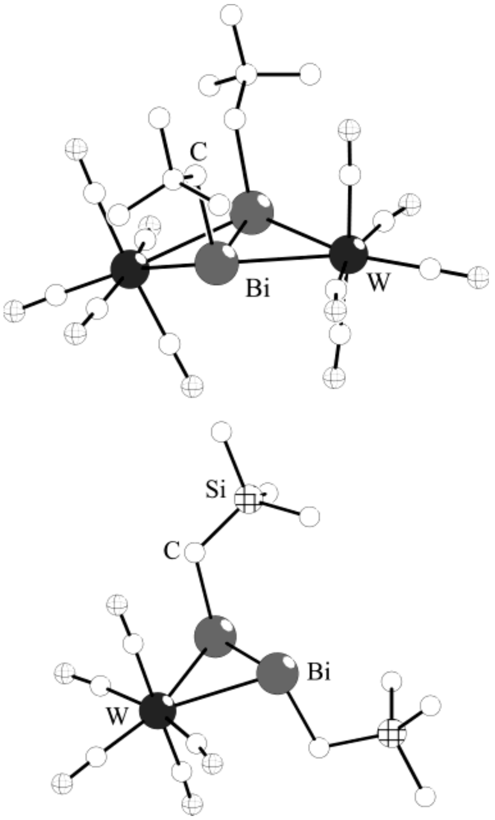


Figure 4. Structures of *cis*−$(RBi)_2[W(CO)_5]_2$ ($R = Me_3CCH_2$) and *trans*−$(RBi)_2W(CO)_5$ ($R = Me_3SiCH_2$) in the crystal state.

These spectral patterns indicate the presence of an effective plane of symmetry with two pairs of chiral antimony atoms. Inversion at antimony can be ruled out at room temperature.

Coordination Chemistry of Neopentyl and (Trimethylsilyl)methyl Antimony and Bismuth Rings. Major chemical differences emerge also when the coordination chemistry of neopentyl and (trimethylsilyl)methyl antimony and bismuth homocycles with the 16-electron complex fragment $W(CO)_5$ is considered. Only the pentastibolane R_5Sb_5 ($R = Me_3SiCH_2$) was found to react as an intact ring ligand with lone-pair donation of one of the antimony atoms to $W(CO)_5$.[20] The trimer−pentamer systems of the bismuth rings R_3Bi_3 and R_5Bi_5 ($R = Me_3CCH_2$, Me_3SiCH_2) react with $W(CO)_5$thf with formation of *cis*-$(RBi)_2[W(CO)_5]_2$ and *trans*-$(RBi)_2W(CO)_5$, two types of dibismuthene complexes with side-on coordination of the ligands.[28,29] The structures of these complexes are shown in Figure 4. The Bi−Bi bond lengths in the 1:2 complexes *cis*-$(RBi)_2[W(CO)_5]_2$ ($R = Me_3CCH_2$, 297.9(7) pm; $R = Me_3SiCH_2$, 300.3(1) pm) are considerably longer than in the 1:1 complex *trans*-$(RBi)_2W(CO)_5$ ($R = Me_3SiCH_2$, 287.69(5) pm), where the double-bond character of the Bi−Bi bond is better preserved. The ready transformation of the bismuth rings into *cis*- or *trans*-dibismuthene ligands illustrates the flexibility and the high reactivity of the system of $(RBi)_n$ oligomers. The results indicate that donation of the electrons involved in the Bi═Bi bond is more efficient for the coordinative bonds to tungsten than donation of a bismuth lone pair of electrons. The relative inertness of the latter is possibly due to the relativistic contraction of the 6s orbitals at bismuth.[9]

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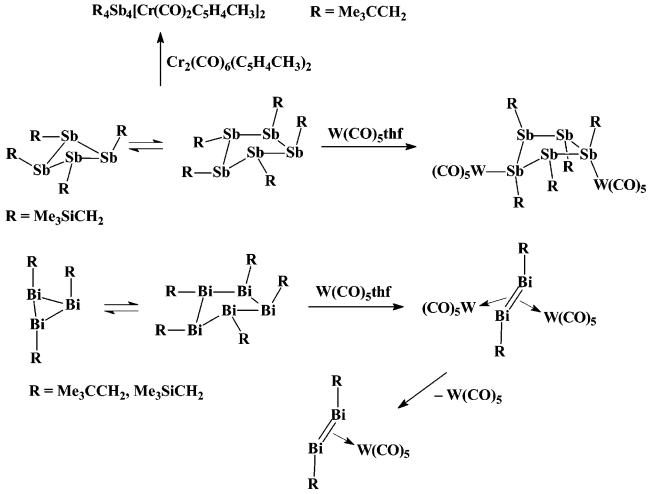
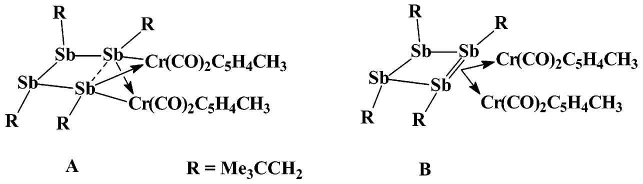
(29) Balázs, L.; Breunig, H. J.; Lork, E. *Angew. Chem.* **2002**, *114*, 2411; *Angew. Chem., Int. Ed.* **2002**, *41*, 2309.

Scheme 11



The coordination to a 15-electron transition-metal complex fragment was studied in the case of the neopentylantimony rings R_nSb_n (R = Me_3CCH_2, *n* = 4, 5). The reaction with $[MeC_5H_4Cr(CO)_3]$ leads to the coordination of a R_4Sb_4 unit on two bridging $MeC_5H_4Cr(CO)_2$ complex fragments (Scheme 11).[21] The antimony ligand in $R_4Sb_4[MeC_5H_4Cr(CO)_2]_2$ can be described as a chain of the type Sb(R)−(SbR)$_2$−(R)Sb coordinating through donation of three electrons per terminal antimony atom to the chromium centers. When the Sb−Sb distance of 2.9737(8) Å between the coordinating antimony atoms is interpreted as corresponding to the structure of the antimony ligand, this can also be viewed as an unsaturated monocycle with side-on coordination through the electrons of a Sb−Sb double bond. Both alternate descriptions are included as formula A and formula B in Chart 1.

Chart 1



Concluding Remarks

Neopentyl and mono- and bis(trimethylsilyl)methyl groups (R) are suitable substituents for the stabilization of a wide variety of low-valent alkylantimony and -bismuth compounds. With these substituents the study of the structures in the solid state and in solution is possible in a temperature range that is easily accessible, even in the case of many of the labile bismuth compounds. Useful starting materials for the syntheses of low-valent alkylantimony and -bismuth compounds are the hydrides REH_2, R_2EH, and R(H)SbSb(H)R and the halides $RECl_2$ and R_2ECl. Comparative studies on $(RE)_n$ (E = Sb, Bi) revealed an unexpected preference for cyclic trimer−pentamer equilibria in the case of the bismuth compounds, whereas tristibiranes are not involved in ring−ring equlibria. Usually the bismuth derivatives are thermally less stable than their antimony analogues. Considerable chemical differences emerge when the coordination chemistry of the ring systems is considered. The complexation of intact homocycles was only achieved in reactions of antimony rings. Analogous dibismuthenes coordinate preferentially through the electrons of the Bi═Bi double bond.

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