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Synthesis, Chemistry, and Structures of Neopentyl and (Trimethylsilyl)methyl Antimony and Bismuth Oligomers

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Dehalogenation of $RSbBr_2$ ($R = Me_3CCH_2$) with Mg gives cyclo-$(RSb)_n$ ($n = 4$ (**1a**), 5 (**1b**)). The compounds cyclo-$(RBi)_n$ ($R = Me_3CCH_2$; $n = 3$ (**2a**), 5 (**2b**)) form by reaction of $RBiCl_2$ with $LiAlH_4$. Equilibria between **1a** and **1b** or between **2a** and **2b** favor the smaller rings at higher temperatures and dilution. Thermal reactions of **2a**,**b** lead to R_4Bi_2 (**3**; $R = Me_3CCH_2$) and elemental bismuth. Reaction of **2a**,**b** with $W(CO)_5(thf)$ (thf = tetrahydrofuran) gives $[\{\mu\text{-}\eta^2\text{-}cis\text{-}(RBi)_2\}\{W(CO)_5\}_2]$ (**4**; $R = Me_3CCH_2$). Decomposition of $[\{\mu\text{-}\eta^2\text{-}cis\text{-}(R'Bi)_2\}\{W(CO)_5\}_2]$ (**5**; $R' = Me_3SiCH_2$) leads to $[\eta^2\text{-}trans\text{-}(R'Bi)_2W(CO)_5]$ (**6**). The crystal structures of **1b**, **4**, and **6** are reported.

Introduction

Relativistic effects[1] should lead to fundamental differences between the reactivity of bismuth(I) compounds and analogous compounds of antimony or the lighter group 15 elements. While true inorganic Bi(I) compounds are still very rare, a number of organometallic examples, e.g. *trans*-dibismuthenes, RBi═BiR ($R = 2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2$, $2,6\text{-}(Me_3C_6H_2)_2C_6H_3$),[2,3] and cyclobismuthines, $(RBi)_n$ ($n = 3$−5; $R = (Me_3Si)_2CH$,[4] $(Me_3Si)_3Si$,[5] Me_3SiCH_2[6]), were recently described and comparison with analogous compounds of the lighter elements has become possible. We found that the bismuth compounds $(RBi)_n$ ($R = (Me_3Si)_2CH$; $n = 3$, 4) exist in solution in a ring−ring equilibrium between the cis,trans trimer and the all-trans tetramer.[4] The analogous cyclostibines have similar structures but different chemistry. They are not transformable into each other in a thermal equilibrium. The tetramer $(RSb)_4$ ($R = (Me_3Si)_2CH$) is stable up to 160 °C.[7] The transformation into the corresponding trimer, $(RSb)_3$, was observed only in an irreversible photochemical reaction.[8] Assuming that in sterically less hindered ring systems the specific properties of analogous Sb(I) and Bi(I) compounds might emerge even more clearly, we chose the (trimethylsilyl)methyl and neopentyl compounds $(RE)_n$ (E = Sb, Bi; $R = Me_3SiCH_2$, Me_3CCH_2) for comparative studies where also aspects of the coordination chemistry of these rings were included. Our previous work showed that the (trimethylsilyl)methyl antimony ring system exists in benzene at ambient temperature mainly as the pentamer, $(Me_3SiCH_2Sb)_5$, and a small fraction of the corresponding tetramer.[9] X-ray diffraction studies revealed that crystals contain exclusively the pentamer, although a full determination of the structure failed due to disorder. The reaction of the (trimethylsilyl)methyl antimony rings with $W(CO)_5(thf)$ in the 1:3 molar ratio results in the coordination of the pentamer in 1,3-$[W(CO)_5]_2(Me_3SiCH_2Sb)_5$.[10] The analogous bismuth ring system $(RBi)_n$ ($R = Me_3SiCH_2$; $n = 3$, 5) is essentially a trimer−pentamer equilibrium in benzene or toluene in the range from −15 to +35 °C, and the reaction with $W(CO)_5(thf)$ gives $[\{\mu\text{-}\eta^2\text{-}cis\text{-}(RBi)_2\}\{W(CO)_5\}_2]$ (**5**; $R = Me_3SiCH_2$ (**5**)), a complex with a *cis*-dibismuthene ligand.[6] The present report features cyclostibines (**1**), cyclobismuthines (**2**), a dibismuthine (**3**), and dibismuthene complexes (**4**−**6**) with neopentyl and trimethylsilylmethyl substituents.

Results and Discussion

The reaction of $Me_3CCH_2SbBr_2$ with Mg in thf gives cyclo-$(Me_3CCH_2Sb)_n$ ($n = 4$ (**1a**), 5 (**1b**)) in 61% yield (Scheme 1). The novel antimony rings are yellow crystalline solids, readily soluble in hydrocarbons and stable under an inert atmosphere for a long time. They were identified by the observation of the molecular ions in the mass spectra, by elemental analyses, by NMR spectra, and by a single-crystal X-ray diffraction study of the five-membered-ring compound **1b**. The ^1H NMR spectra of **1a**,**b** in C_6D_6 at room temperature are depicted in Figure 1.

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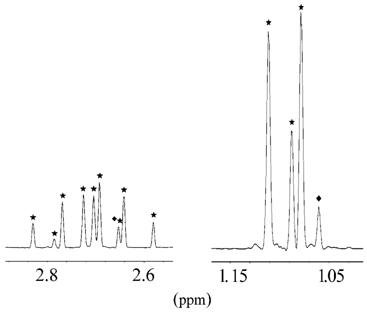
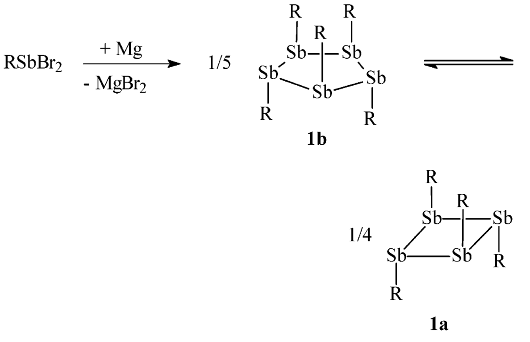


Figure 1. ^{1}H NMR spectra (200 MHz) of (◆) ($Me_3CCH_2Sb)_4$ (**1a**) and (★) ($Me_3CCH_2Sb)_5$ (**1b**) in C_6D_6 at room temperature.

Scheme 1



R = Me_3CCH_2

The spectra contain two singlet signals, one for the CH_3 and one for the CH_2 protons of the antimony four-membered ring **1a** in the all-trans configuration, and three singlet signals in a 2:1:2 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 of the five-membered-ring species **1b**, where the neopentyl groups adopt a maximum of trans positions. The fraction of **1a** increases at the cost of **1b** on dilution in a ring−ring equilibrium (Scheme 1) with the equilibrium constant $[\mathbf{1b}]^4/[\mathbf{1a}]^5 = 1.38 \times 10^{11}$ L mol^{-1} for an overall concentration, [**1a**] + [**1b**], of 2.22×10^{-6} mol L^{-1}. Even at high dilution no signals for a trimer are visible. Characteristic signals for **1a**,**b** are also observed in the ^{13}C NMR spectra. Yellow crystals of **1b** were grown from a solution in petroleum ether at −28 °C, and the structure was determined by X-ray diffraction. The crystals consist of cyclo-($Me_3CCH_2Sb)_5$ molecules. The conformation of the antimony five-membered ring is close to an envelope structure where Sb(1), Sb(2), Sb(3), and Sb(5) lie almost in a plane (mean deviation 0.1690 Å) and Sb(4) is 1.5291 Å above this plane (Figure 2).

The Sb(5)−Sb(1)−Sb(2)−Sb(3) and Sb(2)−Sb(1)−Sb(5)−Sb(4) torsion angles are 18.2(1) and 19.0(1)°, respectively. Two of the neopentyl groups are cis to each other, and three groups are trans to their neighbors. **1b** is the first five-membered organoantimony monocycle (pentastibolane) to be fully characterized by crystal structure analysis. The closest related compounds with known crystal structures are 1,3-[W(CO)$_5$]$_2$($Me_3SiCH_2Sb)_5$[10] and ($Me_3SiCH_2As)_5$,[11] two five-membered rings which adopt *envelope* conformations. The Sb−Sb bond lengths in **1b** are very homogeneous, ranging from 2.812(3) to 2.820(3) Å. They lie in the usual region for Sb−Sb single-bond lengths in cyclostibines (R_4Sb_4 at 2.822(1)−2.878(1) Å[7] and R_3Sb_3 at 2.8188(6)−2.8453(6) Å,[8] R = ($Me_3Si)_2CH$; 1,3-[W(CO)$_5$]$_2$($Me_3SiCH_2Sb)_5$ at 2.818(1)−2.842(1) Å[10]). The Sb−Sb−Sb angles in **1b** fall in two groups; two are narrow (97.3(1) and 95.9(1)° at Sb(3) and Sb(4)) and three are wide (102.4(1), 103.3(1), and 103.9(1)° at Sb(1), Sb(2), and Sb(5)). The Sb−C bond lengths (2.16(3)−2.25(3) Å) and Sb−Sb−C angles (88.8(6)−99.0(1)°) are not unusual. A remarkable feature of the crystal structure of **1b** is the zigzag chain association of the stibolane molecules with intermolecular Sb(3)···Sb(4) contact distances of 4.22 Å, which are close to the sum of van der Waals radii of two Sb atoms (4.4 Å). These weak contacts may be responsible for the avoidance of disorder phenomena, which affected our attempts to determine the structures of ($Me_3SiCH_2Sb)_5$ and **2b**. Close intermolecular Sb···Sb contacts were observed before in the stacks of the ($PhSb)_6$·(solvate) species (4.18−4.23 Å),[12] in the chains of ($MesSb)_4$·(benzene) (3.88 Å),[13] and in distibines, R_2SbSbR_2.[14] Views of the chain association in the crystal structure of **1b** are presented in Figure 3.

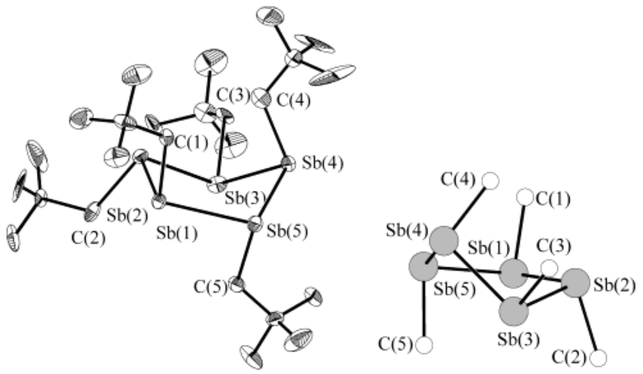


Figure 2. (left) Structure of ($Me_3CCH_2Sb)_5$ (**1b**) in the crystal state. The ellipsoids represent 25% probability. (right) conformation of the Sb core in **1b**. Selected bond lengths (Å) and angles (deg): Sb(1)−Sb(5) = 2.812(3), Sb(1)−Sb(2) = 2.818(3), Sb(2)−Sb(3) = 2.819(3), Sb(3)−Sb(4) = 2.82(3), Sb(4)−Sb(5) = 2.818(3), Sb(1)−C(1) = 2.17(2), Sb(2)−C(2) = 2.25(3), Sb(3)−C(3) = 2.20(2), Sb(4)−C(4) = 2.16(3), Sb(5)−C(5) = 2.21(3); Sb(1)−Sb(2)−Sb(3) = 102.4(1), Sb(5)−Sb(1)−Sb(2) = 103.9(1), Sb(2)−Sb(3)−Sb(4) = 97.3(1), Sb(5)−Sb(4)−Sb(3) = 95.9(1), Sb(1)−Sb(5)−Sb(4) = 103.3(1), C(1)−Sb(1)−Sb(5) = 97.2(6), C(1)−Sb(1)−Sb(2) = 95.5(7), C(2)−Sb(2)−Sb(1) = 96.5(7), C(2)−Sb(2)−Sb(3) = 93.6(7), C(3)−Sb(3)−Sb(2) = 94.3(9), C(3)−Sb(3)−Sb(4) = 92.2(7), C(4)−Sb(4)−Sb(5) = 99.0(1), C(4)−Sb(4)−Sb(3) = 98.4(9), C(5)−Sb(5)−Sb(1) = 88.8(6), C(5)−Sb(5)−Sb(4) = 97.9(8), Sb(1)−Sb(5)−Sb(4) = 103.3(1).

The synthesis of the neopentyl bismuth rings, cyclo-($Me_3CCH_2Bi)_n$ (n = 3 (**2a**), 5 (**2b**)) is achieved by the reaction of $Me_3CCH_2BiCl_2$ with $LiAlH_4$ in Et_2O at −70 °C and decomposition of the intermediate product, $Me_3CCH_2BiH_2$, at about −50 °C (Scheme 2).

The bismuth rings **2a**,**b** are air sensitive and thermally unstable in solution. Removal of the solvent at

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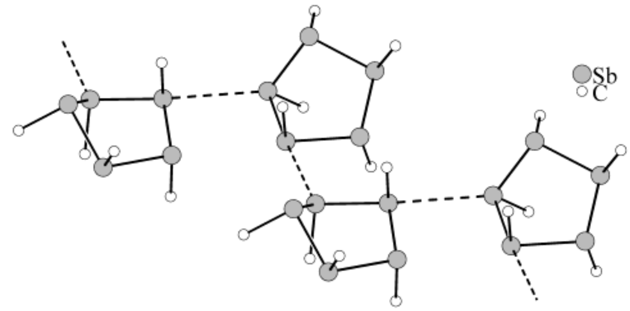


Figure 3. View of the chain association in the crystal structure of (Me$_3$CCH$_2$Sb)$_5$ (**1b**).

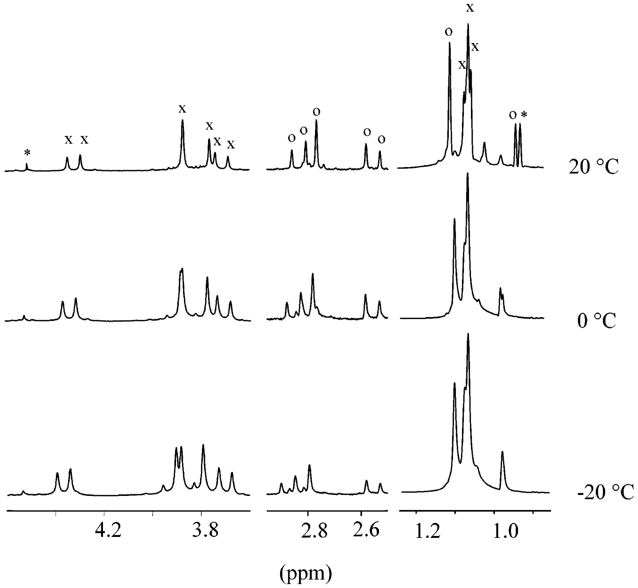
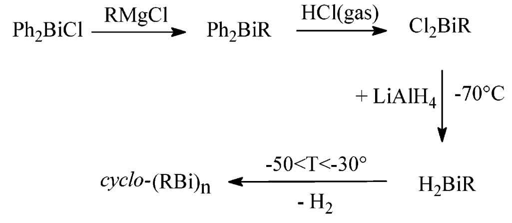


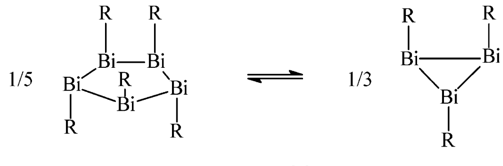
Figure 4. ^{1}H NMR spectra (200 MHz) of (x) (Me$_3$CCH$_2$Bi)$_5$ (**2a**), (o) (Me$_3$CCH$_2$Bi)$_3$ (**2b**), and (*) (Me$_3$CCH$_2$Bi)$_4$ in C$_6$H$_5$CD$_3$.

Scheme 2



R = Me$_3$CCH$_2$; n = 3 (**2a**); n = 5 (**2b**)

Scheme 3



reduced pressure gives a dark red amorphous solid, which is self-igniting in air but stable for months at room temperature under an inert atmosphere. ^{1}H NMR spectra of solutions of **2a**,**b** are shown in Figure 4. The spectra in C$_6$D$_6$ and C$_6$D$_5$CD$_3$ at 20 °C contain two singlet signals in a 1:2 ratio of intensities for the CH$_3$ groups as well as four signals of an AB spin system and a singlet for the CH$_2$ groups of the bismuth three-membered-ring system **2a** in the cis,trans configuration. For the bismuth five-membered-ring compound **2b** there is a complex multiplet signal for the methyl groups. The signals of one of the two diastereotopic CH$_2$ groups of **2b** are isochronic at 20 °C, and therefore, instead of two systems, only one AB spin system and two singlet signals are observed in the methylene region. Like **1b**, **2b** also exists in solution in the configuration with a maximum of trans positions of the substituents with ring inversion between the conformers leading to an effective plane of symmetry. Two additional singlet signals of low intensity result probably from cyclo-(RBi)$_4$. When a solution in C$_6$D$_5$CD$_3$ is cooled, the signals of the five-membered-ring compound **2b** increase in intensity at the cost of those of the three-membered-ring species **2a** and the accidental isochronism in the spectrum of **2b** is abolished. The ring−ring reactions (Scheme 3) are fully reversible between −20 and 20 °C. Below −20 °C the equilibrium is frozen with a **2a**:**2b** molar ratio of 0.3:1. At 45 °C the **2a**:**2b** ratio is 2:1; however, rapid decomposition occurs at this temperature. The values for the equilibrium constant $K = [\mathbf{2a}]^5/[\mathbf{2b}]^3$ are $K = 2.12 \times 10^{-3}$ mol^2 L^{-2} at 20 °C for an overall concentration, [**2a**] + [**2b**], of 1.8×10^{-1} mol L^{-1} and $K = 2.7 \times 10^{-4}$ mol^2 L^{-2} at −20 °C for an overall concentration, [**2a**] + [**2b**], of 2.2×10^{-1} mol L^{-1}.

The red solid obtained by evaporation of the solvent contains probably all the rings with **2b** as the most abundant species. Single crystals grow in acetone at −28 °C. An X-ray structure analysis revealed the exclusive presence of the five-membered-ring species **2b**. However, a full determination of the structure was prevented by disorder phenomena resulting probably from irregular orientations of the five-membered rings.

Thermal decomposition of **2a**,**b** gives the dibismuthine **3** in 60% yield and elemental bismuth (eq 1). **3** is an

$$\underset{\mathbf{2}}{(4/n)\text{cyclo-(RBi)}_n} \rightarrow \underset{\mathbf{3}}{\text{R}_2\text{Bi}{-}\text{BiR}_2} + 2\text{Bi} \qquad (1)$$

$$\text{R} = \text{Me}_3\text{CCH}_2;\ n = 3, 5$$

orange air-sensitive solid, soluble in hydrocarbons. ^{1}H NMR spectra show four signals of an AB spin system and a singlet for the CH$_2$ and CH$_3$ protons. The identity of **3** was also proven by elemental analyses and mass spectra containing the molecular ion.

The reaction of **2a**,**b** with W(CO)$_5$(thf) gives [{μ-η^2-*cis*-(Me$_3$CCH$_2$Bi)$_2$}{W(CO)$_5$}$_2$] (**4**) (eq 2). **4** is a light red

$$\underset{\mathbf{2}}{(2/n)\text{cyclo-(RBi)}_n} + 2\text{W(CO)}_5\text{(thf)} \xrightarrow{-2\text{thf}}$$

$$\underset{\mathbf{4}}{\text{(RBi)}_2[\text{W(CO)}_5]_2} \qquad (2)$$

$$\text{R} = \text{Me}_3\text{CCH}_2;\ n = 3, 5$$

crystalline solid, soluble in organic solvents. Crystals and solutions are air sensitive. ^{1}H NMR spectra of **4** contain two singlet signals: one for the CH$_3$ and the other for the CH$_2$ groups. The fragment M − R appears at **the** highest mass in the mass spectra. The composition was confirmed by high-resolution mass spectro-

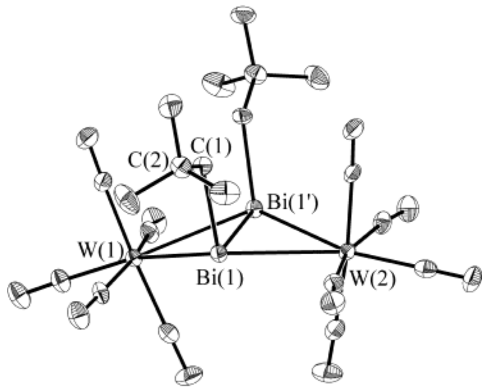


Figure 5. Structure of $(Me_3CCH_2Bi)_2[W(CO)_5]_2$ (**4**) in the crystal state. The ellipsoids represent 30% probability. Selected distances (Å) and angles (deg): Bi(1)−Bi(1′) = 2.9799(7), Bi(1)−C(1) = 2.312(7); Bi(1)−W(1) = 3.1288(7), Bi(1)−W(2) = 3.1411(7); C(1)−Bi(1)−Bi(1′) = 94.5(2), C(1)−Bi(1)−W(1) = 102.8(2), Bi(1′)−Bi(1)−W(1) = 61.6(1), C(1)−Bi(1)−W(2) = 103.8(2), Bi(1′)−Bi(1)−W(2) = 61.7(1), W(1)−Bi(1)−W(2) = 118.2(2).

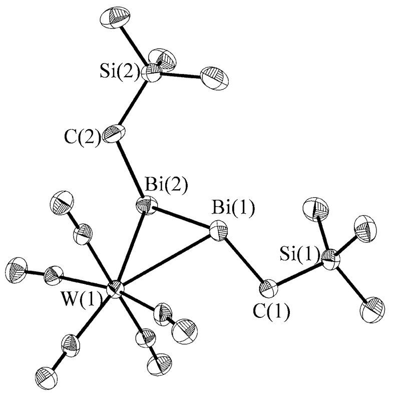


Figure 6. Structure of $[(Me_3SiCH_2Bi)_2W(CO)_5]$ (**6**) in the crystal state. The ellipsoids represent 40% probability. Selected distances (Å) and angles (deg): Bi(1)−Bi(2) = 2.8769(5), Bi(1)−C(1) = 2.284(6), Bi(2)−C(2) = 2.295(6), Bi(1)−W(1) = 3.0701(9), Bi(2)−W(1) = 3.0792(6); C(1)−Bi(1)−Bi(2) = 98.7(2), C(1)−Bi(1)−W(1) = 99.1(2), C(2)−Bi(2)−W(1) = 99.6(2), Bi(2)−Bi(1)−W(1) = 62.3(2), Bi(1)−Bi(2)−W(1) = 62.0(1), C(2)−Bi(2)−Bi(1) = 95.2(2).

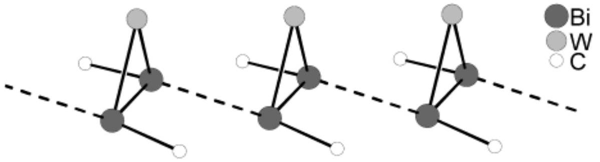
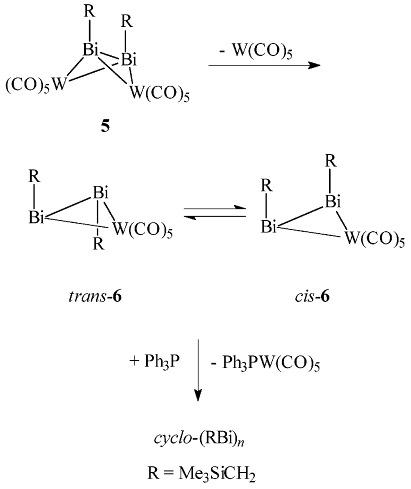


Figure 7. Chain association in the crystal of $[(Me_3SiCH_2Bi)_2W(CO)_5]$ (**6**).

Scheme 4



scopy. The analogous complex $[\{\mu\text{-}\eta^2\text{-}cis\text{-}(Me_3SiCH_2Bi)_2\}\{W(CO)_5\}_2]$ (**5**) was characterized by elemental analyses.[6]

Single crystals of **4** suitable for X-ray diffraction were grown from a petroleum ether solution at −28 °C. They belong to the monoclinic space group $P2_1/m$. The structure of **4** consists of a dibismuthene in the cis form in a bridging position with side-on coordination to two $W(CO)_5$ fragments (1:2 complex). The torsion angle C(1)−Bi(1)−Bi(1′)-C(1′) is 0°. The arrangement corresponds to a bicyclic butterfly structure (Figure 5). The dihedral angles between the Bi_2W planes (154.5°) and the Bi−Bi and Bi−W bond lengths (Bi−Bi = 2.9799(7) Å, Bi−W = 3.1411(7), 3.1288(7) Å) in **4** compare well with the values found in **5** (Bi−W−Bi = 155.5°, Bi−Bi = 3.003(1) Å, Bi−W = 3.118(1), 3.124(1) Å).[6]

Both **4** and the analogous Si compound **5** are unstable in solution at room temperature. For a detailed study of the solution behavior, we chose **5** and found that storing a solution of **5** in organic solvents (benzene, diethyl ether, or petroleum ether) at 20 °C or addition of Ph_3P leads to the removal of a $W(CO)_5$ group and formation of $[(Me_3SiCH_2Bi)_2W(CO)_5]$ (**6**) (Scheme 4). A fraction containing crystals of **6** and **5** was obtained by cooling a solution in petroleum ether to −25 °C. The composition of **6** was confirmed by high-resolution mass spectroscopy. A single-crystal X-ray diffraction study revealed that the structure of solid **6** consists of the trans isomer of RBi═BiR (R = Me_3SiCH_2), side-on coordinated to a $W(CO)_5$ fragment. The molecular structure is shown in Figure 6. The *trans*-dibismuthene ligand is slightly distorted from planarity with a C(1)−Bi(1)−Bi(2)−C(2) torsion angle of −166.1(2)°.

The Bi−Bi bond in **6** (2.8769(5) Å) is significantly shorter than in **5** (3.003(1) Å)[6] and only slightly longer than the Bi−Bi double bonds in uncoordinated dibismuthenes, RBi═BiR (R = $\{(Me_3Si)_2CH\}_3C_6H_2$, 2.8206(8) Å;[2a] R = $(Me_3C_6H_2)_2C_6H_3$, 2.832(1) Å[3a]). Apparently the double-bond character of the Bi−Bi bond of the dibismuthene ligand is essentially preserved in the 1:1 complex **6**, whereas bridging coordination to two $W(CO)_5$ groups in **5** leads to considerable reduction of the bond order. The Bi−W (3.0792(6), 3.0701(9) Å) and Bi−C (2.284(6), 2.295(6) Å) bond lengths as well as the Bi−Bi−C (98.7(2), 95.2(2)°) and C−Bi−W (99.1(2), 99.6(2)°) angles of **6** lie in the usual range. The molecules of **6** are aligned to chains through weak Bi···Bi (4.352(1) Å) contacts which are shorter than the sum of the van der Waals radii of two bismuth atoms (4.80 Å) (Figure 7). Chain association through intermolecular Bi···Bi contacts was also reported for dibismuthines, $R_2Bi{-}BiR_2$.[14]

^1H NMR spectra of a solution of crystals of **6** in C_6D_6 show more signals than expected, although mass spectra of this solution did not contain additional signals. In the NMR spectra, instead of one there are two sets of signals for Me_3SiCH_2 groups. These signals are also observed during the formation of **6** by decomposition of **5**. The ratio of intensities does not significantly change between −70 and +80 °C, but the pattern of one of the

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for 1b, 4, and 6

	1b	**4**	**7**
formula	$C_{25}H_{55}Sb_5$	$C_{20}H_{22}Bi_2O_{10}W_2$	$C_{13}H_{22}Bi_2O_5Si_2W$
fw	964.44	1208.04	916.30
color	yellow	orange	orange
temp (K)	173	173	173
cryst size (mm)	0.5 × 0.25 × 0.1	0.4 × 0.2 × 0.15	0.4 × 0.1 × 0.1
wavelength (Å)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	$P2_1nb$	$P2_1/m$	$P2_1/n$
a (Å)	10.4954(13)	9.456(2)	6.5970(10)
b (Å)	11.8461(16)	12.090(2)	22.702(5)
c (Å)	29.222(9)	12.779(3)	15.422(3)
α (deg)	90	90	90
β (deg)	90	99.17(3)	93.98(3)
γ (deg)	90	90	90
Z	4	2	4
V (Å^3)	3633.2(12)	1442.3(5)	2304.1(8)
d_{calcd} (g cm^{-3})	1.763	2.782	2.782
μ (mm^{-1})	3.680	20.158	20.337
F(000)	1840	1072	1632
θ range (deg)	2.68−25.01	2.33−26.10	2.23−26.10
index ranges	$-1 \le h \le 12$, $-14 \le k \le 1$, $-34 \le l \le 1$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-15 \le l \le 15$	$-8 \le h \le 8$, $-28 \le k \le 27$, $-18 \le l \le 18$
no. of measd data	4344	20 533	22 162
no. of unique data [R(int)]	3659 (R(int) = 0.0606)	2960 (R(int) = 0.0664)	4399 (R(int) = 0.0523)
no. of data/restraints/params	3659/245/289	2960/0/181	4399/0/216
abs cor	empirical (DIFABS)	empirical (DIFABS)	empirical (DIFABS)
R1 ($I > 2\sigma(I)$)	0.0674	0.0237	0.0229
wR2 ($I > 2\sigma(I)$)	0.1177	0.0581	0.0431
R1 (all data)	0.1359	0.0329	0.0374
wR2 (all data)	0.1493	0.0607	0.0464
goodness of fit on F^2	1.019	1.057	0.914
max, min residual density (e Å^{-3})	1.633, −1.132	1.325, −1.101	0.816, −0.769

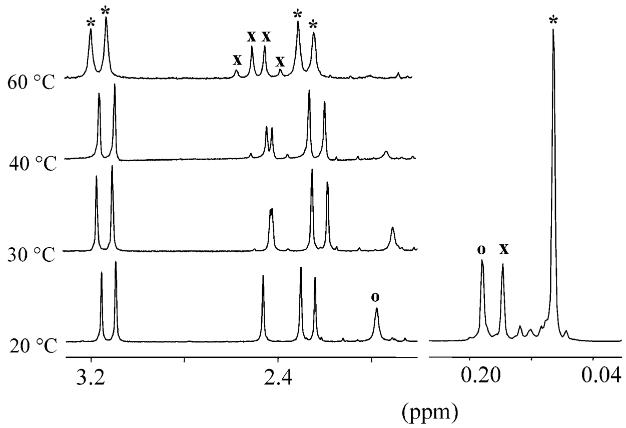


Figure 8. ^{1}H NMR spectra (200 MHz) of (o) [(Me$_3$SiCH$_2$-Bi)$_2${W(CO)$_5$}$_2$] (**5**) and [(Me$_3$SiCH$_2$Bi)$_2$W(CO)$_5$] (**6**; (x) cis form, (*) trans form).

CH$_2$ signals is temperature dependent (Figure 8). A straightforward interpretation of these data is to assume the presence not only of the trans but also of the cis isomers of **6** in solution. The more intense signals are assigned to the trans form, which should be more stable and is prevailing in the crystalline state. Cis−trans isomerization has also been observed in the chemistry of diphosphene complexes. However, photochemical methods are required.[15] Removal of the tungsten carbonyl unit from **5** with formation of Ph$_3$PW(CO)$_5$ and (Me$_3$SiCH$_2$Bi)$_n$ (n = 3, 5)[6] is achieved by addition of excess Ph$_3$P. In a ^{1}H NMR study in C$_6$D$_6$ also the thermal decomposition of **4** was studied, and signals assignable to the cis and trans isomers of [(Me$_3$CCH$_2$-Bi)$_2$W(CO)$_5$] were observed.

Conclusions

With (RE)$_n$ (E = Sb, Bi; R = Me$_3$CCH$_2$, Me$_3$SiCH$_2$, (Me$_3$Si)$_2$CH) there are now three pairs of ring systems available for comparative studies, and characteristic differences between analogous Sb and Bi monocycles are emerging. All three bismuth ring systems take part in ring−ring equilibria with pronounced preferences for the trimers in solution. In contrast, there are no antimony trimers (tristibiranes) involved in equilibria. A common feature of the antimony and bismuth ring systems is the existence of pentamers (R = Me$_3$CCH$_2$, Me$_3$SiCH$_2$) or tetramers (R = (Me$_3$Si)$_2$CH) in the crystalline state. Reactions with W(CO)$_5$(thf) again reveal fundamental differences. The cyclostibines (RSb)$_n$ (R = Me$_3$SiCH$_2$, (Me$_3$Si)$_2$CH) coordinate as intact cyclic ligands, whereas the bismuth rings (RBi)$_n$ (R = Me$_3$SiCH$_2$, Me$_3$CCH$_2$) are readily transformed into dibismuthene ligands.

Experimental Section

General Comments. All the syntheses were carried out under an argon atmosphere using dried solvents distilled under argon prior to use. The NMR spectra were recorded on a Bruker DPX 200 instrument. For the mass spectrometry a Finnigan MAT 8222 instrument was used, and for IR spectra a FT-IR SPEKTRUM 1000 instrument was employed.

X-ray Crystallography. Table 1 contains a summary of the structural analyses reported in this paper. Data for **1b** were collected on a Siemens P4 four-circle diffractometer. For **4** and **7** the data were collected using a STOE IPDS diffractometer. In both cases a graphite monochromator with the

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[15] Yoshifuji, M.; Hashida, T.; Inamoto, N.; Hirotsu, K.; Horiuchi, T.; Higuchi, T.; Ito, K.; Nagase, S. *Angew. Chem.* **1985**, *97*, 230; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 211.

wavelength (Mo Kα) 0.710 73 Å was used. The crystals were attached with Kel-F oil to a glass fiber and cooled under a nitrogen stream at 173 K. The structures were solved by direct methods (full-matrix least squares on F^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. For structure solution and refinement the software package SHELX-97 was used.[16] The drawings were created by the Diamond program from Crystal Impact GbR.[17]

$(Me_3CCH_2Sb)_n$ (n = 4 (1a), 5 (1b)). A solution of 18.25 g (51.8 mmol) $Me_3CCH_2SbBr_2$ in 80 mL of thf was added dropwise to 1.37 g (56.9 mmol) of Mg covered with 20 mL of thf. The reaction mixture was stirred for 12 h at room temperature, at which point the color changed from yellow to brown. The thf was evaporated at low pressure, and the resulting residue was extracted with petroleum ether (4 × 80 mL). Concentration of the solutions and cooling to −28 °C gave 6.1 g (60.9%) of cyclo-$(Me_3CCH_2Sb)_n$ as a yellow-brown crystalline solid, mp 128−129 °C. Single crystals of **1b** were grown from a petroleum ether solution at −28 °C over 4 weeks. Anal. Calcd for $C_{25}H_{55}Sb_5$ (964.50): C, 31.13; H, 5.75. Found: C, 30.89; H, 5.66. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): for **1b**, δ 1.07 (s, $^1J_{CH}$ = 124.5 Hz, 18H; CH_3), 1.08 (s, $^1J_{CH}$ = 124.3 Hz, 9H; CH_3), 1.10 (s, $^1J_{CH}$ = 123.6 Hz, 18H; CH_3), AB spin system with A at 2.60 and B at 2.78 ($^2J_{HH}$ = 12.38 Hz, 4H; CH_2), 2.68 (s, 2H; CH_2), AB spin system with A at 2.67 and B at 2.73 ($^2J_{HH}$ = 10.72 Hz, 4H; CH_2); for **1a**, δ 1.05 (s, 9H; CH_3), 2.64 (s, 2H; CH_2). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): for **1b**, δ 29.61 (s, CH_2), 29.65 (s, CH_2), 31.17 (s, CH_2), 31.66 (s, CH_3), 31.87 (s, CH_3), 32.04 (s, CH_3), 32.35 (s, CMe_3), 32.46 (s, CMe_3), 32.52 (s, CMe_3); for **1a**, δ 29.37 (s, CH_2), 31.51 (s, CMe_3), 32.36 (s, CH_3). MS (EI, 70 eV; *m/z* (relative intensity, %)): 964 (6) [$R_5Sb_5^+$], 893 (18) [$R_4Sb_5^+$], 768 (6) [$R_4Sb_4^+$], 701 (9) [$R_3Sb_4^+$], 71 (100) [R^+] (R = Me_3CCH_2).

$(Me_3CCH_2Bi)_n$ (n = 3 (2a), 5 (2b)). A Grignard solution prepared from 4.08 g (38.3 mmol) of Me_3CCH_2Cl and 2.4 g (65.0 mmol) of Mg in 110 mL of thf was added dropwise to a suspension of 13.74 g (34.4 mmol) of Ph_2BiCl in 100 mL of thf. The reaction mixture was stirred for 2 h at 0 °C and 18 h at room temperature. The thf was removed under vacuum, and the residue was extracted with petroleum ether. After removal of the solvent 8.46 g (56.6%) $Me_3CCH_2BiPh_2$ remained as a yellowish oil. Injection of HCl gas for 2 h at 0 °C into a solution of 8.46 g (19.5 mmol) of $Me_3CCH_2BiPh_2$ in 100 mL of $CHCl_3$, stirring for 30 min, and removal of the solvent gave 5.45 g of a yellowish solid consisting of $Me_3CCH_2BiCl_2$. ^1H NMR (200 MHz, $(CD_3)_2SO$, 25 °C, TMS): δ 1.91 (s, 9H; CH_3), 2.30 (s, 2H; CH_2), ^{13}C NMR (50 MHz, $(CD_3)_2SO$, 25 °C, TMS): δ 34.24 (s, CH_2), 36.46 (s, CH_3), 37.04 (s, CMe_3), MS (70 eV): *m/z* (%): 351 (52) [M^+], 280 (25) [$M^+ - 2Cl$], 209 (10) [Bi^+], 71 (100) [R^+] and $BiCl_3$, MS (70 eV): *m/z*: 314 [M^+], as impurity (<10%). This solid was solved in 150 mL of Et_2O and cooled to −70 °C. Portionwise addition of 1.81 g (47.6 mmol) of $LiAlH_4$ to the precooled (−70 °C) solution, stirring for 4 h, and filtration at −30 °C through a precooled frit covered with Kieselguhr gave a dark red-brown solution of **2**. After the removal of the solvent under vacuum 3.58 g (82.3%) of **2** remained as a red-brown solid, mp 60−62 °C. Anal. Calcd for $C_{25}H_{55}Bi_5$ (1400.61): C, 21.44; H, 3.96. Found: C, 21.28; H, 4.05. ^1H NMR (200 MHz, C_6D_6, 5 °C, TMS): for **2a**, δ 0.95 (s, 9H; CH_3), 0.96 (s, 18H; CH_3), 2.81 (s, 2H; CH_2), AB spin system with A at 2.59 and B at 2.88 ($^2J_{HH}$ = 10.58 Hz, 4H; CH_2); for **2b**, δ 1.06 (s, 18H; CH_3), 1.07 (s, 18H; CH_3), 1.08 (s, 9H; CH_3), 3.79 (s, 2H; CH_2), 3.89 (s, 4H; CH_2), AB spin system with A at 3.73 and B at 4.35 ($^2J_{HH}$ = 10.8 Hz, 4H; CH_2).

$(Me_3CCH_2)_4Bi_2$ (3). A solution of 1.50 g (1.78 mmol) of **2a**,**b** in 50 mL of Et_2O was stirred for 24 h at room temperature, filtered through a frit covered with Kieselguhr, concentrated, and cooled to −28 °C, at which point 0.61 g (64%) of orange-red crystals of **3** formed, mp 72−74 °C. Anal. Calcd for $C_{20}H_{44}Bi_2$ (702.53): C, 34.19; H, 6.31. Found: C, 33.77; H, 6.38. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 1.11 (s, 9H; CH_3), AB spin system with A at 2.40 and B at 3.26 ($^2J_{HH}$ = 10.8 Hz, 2H; CH_2). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 31.83 (s, CMe_3), 33.33 (s, CH_2), 33.39 (s, CH_3). MS (EI, 70 eV; *m/z* (relative intensity, %)): 702 (25) [M^+], 631 (18) [$M^+ - R$], 560 (6) [$M^+ - 2R$], 351 (42) [R_2Bi^+], 71 (100) [R^+] (R = Me_3CCH_2).

$(Me_3CCH_2Bi)_2[W(CO)_5]_2$ (4). A solution of 0.13 g (0.31 mmol) of $W(CO)_5(thf)$ in 100 mL of thf was added to 0.26 g (0.31 mmol) of **2** in 10 mL of thf at 0 °C. After the mixture was stirred for 3 h at 0 °C, the solvent was removed and the residue was extracted with 50 mL of petroleum ether. The extracts were filtered through a frit covered with Kieselguhr. Concentrating and cooling the solution to −28 °C gave 0.25 g (65.7%) of light red crystals of **4**, mp 86−88 °C dec. HRMS (*m/z*): [$M^- - R$] calcd, 1 132.892 46; found, 1132.8925; R = 6000. ^1H NMR (200 MHz, C_6D_6, 25 °C, TMS): δ 1.04 (s, 9H; CH_3), 2.69 (s, 2H; CH_2). ^{13}C NMR (50 MHz, C_6D_6, 25 °C, TMS): δ 32.93 (s, CH_2), 33.24 (s, CH_3), 33.36 (s, CMe_3), 190.0 (s, CO), 192.1 (s, CO). IR (Nujol): 2053, 1948 cm^{-1} (ν(CO)). MS (EI, 70 eV; *m/z* (relative intensity, %)): 1135 (2) [$M^+ - R$], 884 (25) [$M^+ - W(CO)_5$], 813 (35) [$RBi_2W(CO)_5^+$], 742 (25) [$Bi_2W(CO)_5^+$], 729 (12) [$RBi_2W(CO)_2^+$], 714 (20) [$Bi_2W(CO)_4^+$], 701 (15) [$RBi_2W(CO)^+$], 686 (15) [$Bi_2W(CO)_3^+$], 673 (12) [RBi_2W^+], 658 (14) [$Bi_2W(CO)_2^+$], 636 (15) [$Bi_2W(CO)^+$], 602 (10) [Bi_2W^+], 209 (10) [Bi^+], 71 (100) [R^+] (R = Me_3CCH_2).

$(Me_3SiCH_2Bi)_2W(CO)_5$ (6). A solution of 0.97 g (0.78 mmol) of $(Me_3SiCH_2Bi)_2[W(CO)_5]_2$ (**5**)[6] in 50 mL of petroleum ether was stirred at room temperature for 36 h and filtered through a frit covered with Kieselguhr. After the solution was concentrated, it was cooled to −28 °C and crystals of **5** precipitated as the first fraction. The second fraction contained **5** and 0.1 g (14%) of red crystals of *trans*-**6**, mp 71−73 °C. HRMS (*m/z*): [M^+] calcd, 914.009 58; found, 914.007 18; R = 10 000. ^1H NMR (200 MHz, C_6D_6, 25 °C): for *trans*-**6**, δ 0.08 (s, 9H; CH_3), AB spin system with A at 2.24 and B at 3.11 ($^2J_{HH}$ = 12.22 Hz, 2H; CH_2); for *cis*-**6**, δ 0.14 (s, 9H; CH_3), 2.44 (s, 2H; CH_2). IR (Nujol): 2059, 1956 cm^{-1} (ν(CO)). MS (EI, 70 eV; *m/z* (relative intensity, %)): 916 (55) [M^+], 829 (100) [$M^+ - R$], 773 (42) [$RBiW(CO)_4^+$], 745 (78) [$RBiW(CO)_3^+$], 742 (25) [$Bi_2W(CO)_5^+$], 717 (40) [$RBiW(CO)_2^+$], 714 (20) [$Bi_2W(CO)_4^+$], 687 (40) [$RBiW(CO)^+$], 658 (20) [$Bi_2W(CO)_2^+$], 505 (18) [RBi_2^+], 418 (10) [Bi_2^+] 209 (10) [Bi^+], 87 (29) [R^+], (R = Me_3SiCH_2).

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and *U* values, bond distances and angles, anisotropic thermal parameters, and dihedral angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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