116 *Inorg. Chem.* **1995,** *34,* 116−119

Antimony(V) and Bismuth(V) Methyl Compounds: A Structural Comparison

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Received May 26, 1994[⊗]

Crystal structures at low temperatures of $Sb(CH_3)_5$ (a = 663.0(2), b = 1100.4(3), c = 1109.0(3) pm; Z = 4; *Ccmm*), $Sb(C_6H_5)_3(CH_3)_2$ (a = 1527.9(2), b = 791.2(1), c = 1781.7(3) pm; β = 104.59(1)°; Z = 4; $P2_1/c$), and $Li^+(THF)_4Sb(CH_3)_6^-$ (a = 1785.7(6), b = 852.5(3), c = 1261.7(5) pm; β = 134.74(4)°; Z = 2; *C*2/*m*) are presented and compared with those of recently prepared $Bi(CH_3)_5$ and $Li^+(THF)_4Bi(CH_3)_6^-$. All pentacoordinated compounds have very regular trigonal bipyramidal structures, in contrast to $Sb(C_6H_5)_5$ and $Bi(C_6H_5)_5$. Differences between axial and equatorial bond lengths are pronounced in antimony compounds, but not so in violet $Bi(CH_3)_5$. Colorless $Li(THF)_4{}^+Sb(CH_3)_6^-$ and orange $Li(THF)_4{}^+Bi(CH_3)_6^-$ have octahedral anions, with averaged bond lengths of 223.5(5) pm (Sb−C) and 233(1) pm (Bi−C).

Introduction

Pentamethylantimony, $Sb(CH_3)_5$, was described in 1953 as a colorless liquid. Its structure determination in the gas and solid phases presented a long-lasting problem. Vibrational spectra are in accord with a bipyramidal structure.[1] According to the same method, $Sb(c\text{-}C_3H_5)_5$ is said to have a square pyramidal structure,[2] as does $Sb(C_6H_5)_5$ in the solid state,[3] whereas in the adduct $Sb(C_6H_5)_5 \cdot {}^1/_2C_6H_{12}$[4] and in $Sb(p\text{-}C_6H_4CH_3)_5$[5] trigonal bipyramidal structures are observed. As late as 1992 the trigonal bipyramidal structure was confirmed for $Sb(CH_3)_5$ in the gas phase by electron diffraction.[6] $As(CH_3)_5$ was prepared in 1973 and supposedly has the same structure, according to its vibrational spectra.[7] While $N(CH_3)_5$ and $P(CH_3)_5$ obviously do not exist so far, we succeeded recently in preparing $Bi(CH_3)_5$ as a violet, crystalline solid, stable only below −100 °C.[8] The structure was found to be trigonal bipyramidal, and now the solid state structures of $Sb(CH_3)_5$ and $Bi(CH_3)_5$ can be compared, including details of bond lengths and angles.

The question as to whether the trigonal bipyramidal structure of $Sb(CH_3)_5$ or the square pyramidal structure of $Sb(C_6H_5)_5$ will prevail in a mixed compound will be answered by the synthesis and crystal structure of $Sb(C_6H_5)_3(CH_3)_2$.

The existence of the $Sb(CH_3)_6^-$ anion in equilibrium with $Sb(CH_3)_5$ and CH_3Li in solution was postulated by Wittig as early as 1953; it was shown that only excess CH_3Li beyond the 1:1 composition resulted in a strongly positive Gilman test, but by distillation it was found that the solution liberates $Sb(CH_3)_5$.[9] The bismuth counterpart $Bi(CH_3)_6^-$ has been known since 1994.[8] At the beginning of this work it was not absolutely certain that these compounds have an octahedral structure, because $W(CH_3)_6$[10] and $Zr(CH_3)_6^{2-}$ [11] are trigonal prismatic. This deviation from the overwhelming number of octahedral structures is at present not fully understood. At least, we hoped to clarify whether this peculiar behavior is a special feature of transition metal elements.

Experimental Section

General Procedures. All manipulations and reactions were carried out under argon in carefully dried solvents.

Diethyl ether and THF were dried by sodium and molecular sieves. NMR spectra were recorded on a JEOL FT 90 Q multinuclear spectrometer at 89.55 MHz for ^1H.

$Sb(CH_3)_3Br_2$ and $Sb(C_6H_5)_3Cl_2$ were prepared as previously described.[12]

$Sb(CH_3)_5$. A 21 mmol sample of $Sb(CH_3)_3Br_2$ was dissolved in 50 mL of diethyl ether. Then 44 mmol of CH_3Li in a diethyl ether solution was added at −70 °C. After this mixture was warmed to −10 °C within 1.5 h, the solvent was removed under vacuum at −40 to −60 °C. The oily residue and the removed diethyl ether were fractionally condensed using dynamic high vacuum. Working at low temperatures and trap-to-trap distillation of the ether increase the yield to 96% as compared to 63% in the original preparation.[9] Suitable crystals were grown by sublimation under vacuum in sealed glass ampules by using a small temperature gradient around −78 °C.

$Sb(C_6H_5)_3(CH_3)_2$. To a suspension of 4.7 mmol of $Sb(C_6H_5)_3Cl_2$ in 10 mL of diethyl ether was added at −78 °C 9.6 mmol of methyllithium in a diethyl ether solution. The reaction mixture was stirred about 30 min at this temperature. Then the mixture was allowed to warm slowly until a colorless precipitate began to form. Immediately afterward it was cooled again to −78 °C, and the precipitate was filtered off and dried under vacuum at room temperature. The compound was a colorless solid that decomposed around 70 °C. ^1H-NMR (acetone-d_6): δ 7.25 (m, 15 H), 1.56 (s, 6H). Mass spectrum (80 eV, EI): m/z = 367 ($^{121}Sb(C_6H_5)_3CH_3^+$), 305 ($^{121}Sb(C_6H_5)_2(CH_3)_2^+$), and smaller fragments. Suitable crystals were obtained by dissolution in acetone at room temperature, filtering off, and recrystallization at −78 °C.

Lithium Hexamethylantimonate−THF Complex, $Li(THF)_4{}^+Sb(CH_3)_6^-$. A 2.9 mmol sample of CH_3Li in a diethyl ether solution was added to 2.7 mmol of $Sb(CH_3)_5$, dissolved in 5 mL of THF at −78 °C. A colorless suspension was obtained and warmed to room temperature. The clear solution was transferred through a thin Teflon

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1994.

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Table 1. Crystal Data and Experimental Details

	$Sb(CH_3)_5$	$Sb(C_6H_6)_3(CH_3)_2\cdot CH_3COCH_3$	$Li(C_4H_8O)_4^+$-$Sb(CH_3)_6^-$
mol wt	196.92	435.17	483.31
a, pm	663.0(2)	1527.9(2)	1785.7(6)
b, pm	1100.4(3)	791.2(1)	852.5(3)
c, pm	1109.0(3)	1781.7(3)	1261.7(5)
α, deg	90	90	90
β, deg	90	104.59(1)	134.74(4)
γ, deg	90	90	90
V, 10^6 pm^3	809.1(4)	2084.3(6)	1364.7(1)
space group	*Ccmm* (No. 63)	$P2_1/c$ (No. 14)	*C*2/*m* (No. 12)
Z	4	4	2
temp, °C	−143	−147	−143
scan method	$\omega-\theta$	$\omega-2\theta$	$\omega-\theta$
θ min−max, deg	3−35	2−25	3−30
octants	$-h,k,\pm l$	$\pm h,+k,+l$	$h,k,\pm l$
no. of measd reflns	1989	7613	2168
no. of indep reflns	969	6971	2106
no. of $I > 3\sigma(I)$ reflns	881	6172	2084
no. of params	27	307	117
abs cor	DIFABS	DIFABS	DIFABS
μ, mm^{-1}	35.75	14.1	10.9
F(000)	384.0	896.0	486.0
R(int)	0.020	0.015	0.024
R	0.022	0.024	0.038
R_w	0.021	0.021	0.036

Table 2. Positional and Equivalent Isotropic Thermal Parameters for $Sb(CH_3)_5$

atom	*x*	*y*	*z*	*B*, 10^4 pm^2	s.o.f.[a]
Sb	0.8315(0)	0.0000(0)	0.7500(0)	1.49	0.25
C1	1.1528(7)	0.0000(0)	0.7500(0)	2.64	0.25
C2	0.6714(8)	−0.1256(5)	0.8630(5)	2.67	0.50
C3	0.8303(9)	0.1353(5)	0.8988(5)	2.95	0.50

[a] Site occupation factor.

tube into a glass ampule. After sealing of the ampule, colorless crystals were obtained at about −70 °C.

Crystallographics

Crystals were mounted at −50 °C on an Enraf-Nonius CAD 4 diffractometer (Mo Kα radiation, graphite monochromator, and a cooling equipment for the temperature range between −143 and −163 °C using a special low-temperature crystal-mounting device as described previously[13,14]). Lattice constants were established by fine orientation of 25 reflections with 20° < θ < 25°. X-ray reflection intensities were measured in a conventional way by scanning across the reflection allowing 10−100 s for each reflection (one-fourth of this time was used for background measurement). After the usual Lorentz and polarization corrections, the structure was solved by the heavy-atom method. Light atoms were found in difference Fourier maps.[15] After the absorption correction,[16] all atoms were refined anisotropically. In the case of $Sb(C_6H_5)_3(CH_3)_2$, hydrogen atoms were refined isotropically with a fixed vibrational parameter of 0.3 Å^2. In the cases of $Sb(CH_3)_5$ and $Sb(CH_3)_6^-$, hydrogen atoms could only be partially found, and also because of symmetry-enforced disorder they were not included into the refinement. For details of the crystallographic measurements, see Table 1; results are given in Tables 2−4.

Results

Comparison of $Bi(CH_3)_5$ and $Sb(CH_3)_5$. $Bi(CH_3)_5$ is prepared similarly to $Sb(CH_3)_5$. Its thermal lability above −100 °C and the thermal lability of its precursor $Bi(CH_3)_3Cl_2$ above −30 °C probably prevented its earlier detection. Structurally $Bi(CH_3)_5$ and $Sb(CH_3)_5$ are very similar; lattice constants, space groups, and atomic parameters differ so little that it is possible that both compounds form mixed crystals. This, however, was not investigated. The solution of the cyrstal structures was accompanied by a difficult space group problem. $C222_1$ (No. 20), $Ccm2_1$ (No. 36), *Cc*2*m* (No. 40), and *Ccmm* (No. 63) were possible according to absent conditions; in fact, the structures of both compounds could be solved in all these space groups, resulting in the same model containing disordered carbon atoms. Therefore the space group of highest symmetry *Ccmm* was finally chosen, which dictates the disorder described below. The resulting molecule in disordered fashion is shown in Figure 1. From the predominant angles close to 90, 180, and 120° it was clear that the building principle is the trigonal bipyramid. The disorder is equivalent to a rotation of 90° around the bond formed by the nondisordered Sb (Bi) and equatorial C atoms. Hydrogen atoms could be located only partially, and since they are disordered also, they were not included in the refinement.

Table 3. Positional and Equivalent Isotropic Thermal Parameters for $(C_6H_5)_3Sb(CH_3)_2\cdot CH_3COCH_3$

atom	*x*	*y*	*z*	*B*, 10^4 pm^2
Sb	0.0867(0)	0.4831(0)	0.8535(0)	1.32
C01	0.0466(2)	0.6513(3)	0.5846(1)	3.35
C02	0.1453(2)	0.6431(2)	0.5916(1)	2.63
C03	0.1837(2)	0.4756(3)	0.5801(2)	4.25
C4	0.1899(1)	0.5684(3)	0.8012(1)	2.07
C5	0.0915(1)	0.2632(3)	0.9235(1)	2.28
C11	0.1497(1)	0.6353(2)	0.9589(1)	1.63
C12	0.1086(1)	0.7756(2)	0.9839(1)	1.82
C13	0.1513(1)	0.8643(2)	1.0505(1)	2.19
C14	0.2362(1)	0.8157(2)	1.0934(1)	2.18
C15	0.2786(1)	0.6791(2)	1.0696(1)	2.12
C16	0.2360(1)	0.5902(2)	1.0030(1)	1.94
C21	0.0287(1)	0.3281(2)	0.7461(1)	1.62
C22	−0.0554(1)	0.3552(2)	0.6948(1)	1.87
C23	−0.0846(1)	0.2620(2)	0.6266(1)	2.14
C24	−0.0292(1)	0.1373(3)	0.6087(1)	2.48
C25	0.0545(1)	0.1062(3)	0.6588(1)	2.58
C26	0.0824(1)	0.2009(2)	0.7265(1)	2.19
C31	−0.0322(1)	0.6350(2)	0.8299(1)	1.46
C32	−0.1098(1)	0.5809(2)	0.8498(1)	1.76
C33	−0.1879(1)	0.6788(2)	0.8308(1)	2.05
C34	−0.1884(1)	0.8306(2)	0.7920(1)	2.19
C35	−0.1109(1)	0.8875(2)	0.7734(1)	2.17
C36	−0.0332(1)	0.7897(2)	0.7922(2)	1.94
O	0.1920(1)	0.7684(2)	0.6056(1)	3.86

Table 4. Positional and Equivalent Isotropic Thermal Parameters for $[Li(C_4H_8O)_4]^+[Sb(CH_3)_6]^-$

atom	*x*	*y*	*z*	*B*, 10^4 pm^2	s.o.f.[a]
Sb	0.0000(0)	0.5000(0)	0.0000(0)	1.41	0.25
Li	0.5000(0)	0.2526(18)	0.5000(0)	2.27	0.25
C1	0.0833(4)	0.5000(0)	0.9270(5)	3.52	0.50
C2	0.1552(4)	0.5000(0)	1.2399(5)	3.64	0.50
C3	0.0000(0)	0.2386(6)	0.0000(0)	3.93	0.50
O1	0.5224(3)	0.3713(7)	0.6474(5)	3.01	0.50
C11	0.4434(5)	0.4668(12)	0.6175(8)	3.91	0.50
C12	0.4960(7)	0.6234(12)	0.6934(10	3.82	0.50
C13	0.6081(6)	0.5688(12)	0.8330(10	3.76	0.50
C14	0.6250(6)	0.4206(12)	0.7885(9)	3.37	0.50
O2	0.6249(4)	0.1299(6)	0.6022(5)	3.30	0.50
C21	0.6672(7)	0.0862(11)	0.5431(9)	3.85	0.50
C22	0.7320(8)	0.9397(11)	0.6260(10	4.24	0.50
C23	0.7047(9)	0.8855(13)	0.7092(13	5.30	0.50
C24	0.6753(7)	0.0399(12)	0.7324(9)	5.10	0.50

[a] Site occupation factor

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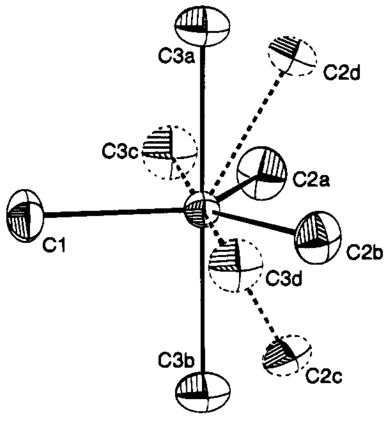

Figure 1. ORTEP drawing of the disordered $Sb(CH_3)_5$ molecule, with thermal ellipsoids shown at the 50% probability level. Broken atoms indicate the second orientation of the 2-fold disordered molecule. Except for slightly larger vibrational amplitudes, the $Bi(CH_3)_5$ molecule is practically identical.[8]

Table 5. Selected Bond Lengths (pm) and Bond Angles (deg) for $Sb(CH_3)_5$[a] and $Bi(CH_3)_5$[b]

	Lengths		
Sb–C1	213.0(5)	Bi–C1	230(2)
Sb–C2	214.6(5)	Bi–C2	227(1)
Sb–C3	222.2(5)	Bi–C3	228(2)
	Angles		
C1–Sb–C2	119.6(1)	C1–Bi–C2	119.3(5)
C1–Sb–C3	90.2(1)	C1–Bi–C3	89.9(5)
C2a–Sb–C2b	120.8(1)	C2a–Bi–C2b	121.4(9)
C2–Sb–C3	89.8(2)	C2–Bi–C3	90.4(6)
C3a–Sb–C3b	179.6(3)	C3a–Bi–C3b	179.8(8)

[a] The values differ marginally from those cited in ref 8 because, for better comparison with $Bi(CH_3)_5$, they are taken from a calculation without hydrogen atoms. [b] Values from ref 8.

The trigonal bipyramidal structures of $Sb(CH_3)_5$ and $Bi(CH_3)_5$ differ in one important detail: While in $Sb(CH_3)_5$ axial bonds are considerably longer than equatorial bonds, the differentbonds in $Bi(CH_3)_5$ have almost equal lengths, even if one considers the larger estimated errors in the latter; see Table 5. The difference in axial and equatorial bond lengths can be described as a result of more ligand crowding in the axial position. Alternatively, it may be described as a result of qualitatively different kinds of bonding, namely linear three-center bonding in the axis versus sp^2 hybrid bonding to the equatorial atoms. The fact that, in the case of the larger central atom of bismuth, the difference in bond lengths almost disappears is consistent with the argument of less steric repulsion, whereas the argument of different types of bonding is at least not necessary.

While both compounds are structurally very similar, they differ enormously in stability and color, and these chemical (stability) and physical (color) differences are probably related. The bond lengths of Bi–C versus Sb–C are somewhat larger (about 11 pm on average), but not enough to declare the Bi–C-bonds as particularly weak ones. Certainly the known fact that Bi(V) is a much stronger oxidant than Sb(V) leads to the following explanation: It is the much greater stability of Bi^{III} versus Sb^{III} that favors the decomposition reaction. This stabilization can be explained in terms of a less effective shielding of the Bi nucleus as a result of the filled f shell (lanthanoid contraction) that particularly stabilizes the nonbonding electron pair with high s character Bi^{III}. This effect can be enhanced by the relativistic contraction of orbitals with nonzero electron density close to the nucleus. The relative size of both effects may be estimated.[17]

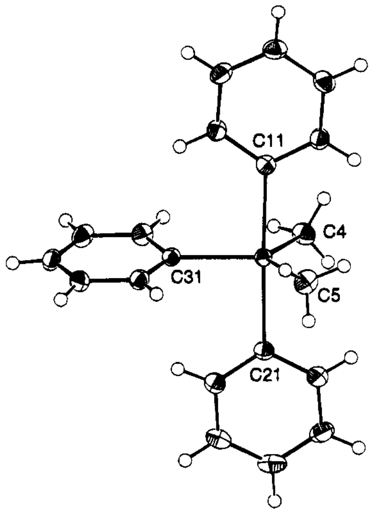

Figure 2. ORTEP drawing of the $(C_6H_5)_3Sb(CH_3)_2$ molecule with thermal ellipsoids shown at the 50% probability level. The cocrystallized acetone molecule is omitted for clarity.

$Bi(C_6H_5)_5$ and its derivatives are all deeply colored, while the corresponding antimony compounds are not. In the case of $Bi(C_6H_5)_5$, the absorption could be associated with the basal bonds of these square pyramids. It was shown by a calculation that the HOMO–LUMO gap of square pyramidal BiH_5 is half the size of that of trigonal bipyramidal BiH_5, because the largely Bi-centered LUMO is lowered by the relativistic effect.[18] The absorption is equivalent to a charge transfer from basal ligands to the bismuth atoms. This charge transfer is enhanced in the case of electron-donating methyl groups so that even in a trigonal bipyramidal structure the material is colored.

Of the now known pentamethyl compounds $As(CH_3)_5$, $Sb(CH_3)_5$, $Bi(CH_3)_5$, and $Ta(CH_3)_5$, only the last is square pyramidal.[6] This discrepancy is paralleled by the structures of six-coordinated methyl compounds; see below. Lack of steric hindrance in the coordination sphere of $Ta(CH_3)_5$ cannot be the reason, as has been proposed, because bismuth is an even larger atom than tantalum. There must be a difference in the bonding between main group and transition compounds. But these differences should be subtle, since $Bi(C_6H_5)_5$ and all of its derivatives with one exception are square pyramidal also.

$Sb(C_6H_5)_3(CH_3)_2$. The preparation and structural investigation of $Sb(C_6H_5)_3(CH_3)_2$ were carried out to determine whether a square pyramidal structure as in $Sb(C_6H_5)_5$ or a trigonal bipyramidal structure as in $Sb(CH_3)_5$ would be found in a compound with these ligands mixed. It would be interesting also to investigate this in the case of bismuth compounds. But while the antimony compound is obtained by the conventional route of reacting $Sb(C_6H_5)_3Cl_2$ with CH_3Li, the corresponding reaction in the bismuth system gave only small amounts of $Bi(C_6H_5)_5$, indicating that ligand scrambling is difficult to suppress here.

The structure of $Sb(C_6H_5)_3(CH_3)_2$ could be refined, including the positions of all hydrogen atoms. The compound is clearly trigonal bipyramidal; see Figure 2 and Table 6. The strong electron-withdrawing phenyl groups are found in axial positions. The angles between the equatorial ligands indicate that methyl groups must be considered larger ligands than phenyl groups in the sense of the valence-shell electron-pair repulsion model. It is interesting to note that all equatorial bond lengths are very

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Table 6. Selected Bond Lengths (pm) and Bond Angles (deg) for $(C_6H_5)_3Sb(CH_3)_2{\cdot}CH_3COCH_3$

	Lengths		
Sb−C4	213.4(2)	Sb−C21	225.8(2)
Sb−C5	213.1(2)	Sb−C31	212.9(2)
Sb−C11	223.5(2)		
	Angles		
C21−Sb−C11	177.7(1)	C4−Sb−C31	115.0(1)
C31−Sb−C11	91.5(1)	C5−Sb−C11	90.2(1)
C31−Sb−C21	90.3(1)	C5−Sb−C21	90.1(1)
C4−Sb−C11	89.3(1)	C5−Sb−C31	118.6(1)
C4−Sb−C21	88.6(1)	C5−Sb−C4	126.4(1)

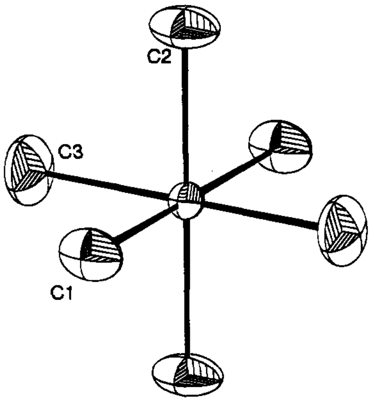

Figure 3. ORTEP drawing of the $Sb(CH_3)_6^-$ anion in $Li(THF)_4^+$-$Sb(CH_3)_6^-$, with thermal ellipsoids shown at the 50% probability level. The $Bi(CH_3)_6^-$ anion is practically identical except for slightly larger vibrational amplitudes.[8]

similar, in spite of the different chemical characters of the ligands.

$Sb(CH_3)_6^-$ and $Bi(CH_3)_6^-$. Pentamethylantimony and -bismuth both react with excess methyllithium forming the corresponding hexamethyl anions $Sb(CH_3)_6^-$ and $Bi(CH_3)_6^-$. $Sb(CH_3)_6^-$ has been mentioned before,[9] while the existence of $Bi(CH_3)_6^-$ was described only recently in a short communication.[8] The colorless antimony compound is stable at room temperature in solution under argon, while the orange bismuth compound decomposes above −60 °C, thus being only marginally more stable than $Bi(CH_3)_5$ itself. The crystal structures of both compounds are again so similar that isomorphism (existence of mixed crystals) would seem to be possible, but this was again not tested. The solution of both crystal structures was difficult due to a disorder of the $Li^+(THF)_4$ cation. The disorder is probably caused by the approximate 5-fold symmetry of the THF molecules. For each THF molecule there are two possible orientations, and the actual position of the oxygen atom dictates the position of the 2-fold disordered Li^+ cation. The anions $Sb(CH_3)_6^-$ and $Bi(CH_3)_6^-$ are clearly octahedral; see Figure 3. In both cases, the bond lengths between central atom and carbon are somewhat longer than even the axial bond lengths in the pentamethyl compounds; see Table 7. This trend is expected.

Table 7. Selected Bond Lengths (pm) and Bond Angles (deg) for $[Li(C_4H_8O)_4]^+[Sb(CH_3)_6]^-$ [a] and $[Li(C_4H_8O)_4]^+[Bi(CH_3)_6]^-$ [b]

	Lengths		
Sb−C1	223.4(4)	Bi−C1	236(1)
Sb−C2	224.4(4)	Bi−C2	233(1)
Sb−C3	222.8(5)	Bi−C3	230(2)
Sb−C[c]	223.5(5)	Bi−C[c]	233(1)
	Angles		
C1−Sb−C2	90.5(2)	C1−Bi−C2	89.6(4)
C1−Sb−C3	90.0(0)	C1−Bi−C3	90.0(0)
C2−Sb−C3	90.0(0)	C2−Bi−C3	90.0(0)

[a] The values differ marginally from those cited in ref 8 because, for better comparison with $Bi(CH_3)_5$, they are taken from a calculation without hydrogen atoms. [b] Values from ref 8. [c] Averaged value.

This is one of the few cases where structural information is known about a main group element with six surrounding carbon ligands. Recently, $Te(CH_3)_6$[19] was prepared, but structural information is to our knowledge not yet known. Also recently, we showed that $Bi(C_6H_5)_6^-$ [20] does exist and has an octahedral structure. These main group compounds thus seem to behave normally, in contrast to the two known cases of transition metal compounds, $Zr(CH_3)_6^{2-}$ and $W(CH_3)_6$, which have a trigonal prismatic structure.[10,11] This deviation from normal behavior is at present not fully understood.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Graduiertenkolleg Synthese und Strukturaufklärung Niedermolekularer Verbindungen. We are grateful to Ms. R. Herbst-Irmer of the University of Göttingen for help with the space group problem of $Sb(CH_3)_5$.

Supplementary Material Available: Tables listing anisotropic thermal parameters, hydrogen positional parameters, and bond distances and angles (3 pages). Ordering information is given on any current masthead page.

IC940603+

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