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Synthesis, Structure, and Reactions of a 10-Sb-4 Type Antimony Ate Complex†

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A 10-Sb-4 type organoantimony ate complex was prepared from hexafluorocumyl alcohol and $SbCl_3$ as an air and water stable compound. Its X-ray structural analysis revealed a distorted pseudo-trigonal bipyamidal structure. The compound reacted with both alkyl halides and organolithium reagents to yield neutral 10-Sb-5 compounds .

It is common knowledge that elements of group XV in and beneath the second row on the periodic table are capable of forming 10-Pn-5(1) type organic compounds and recently a considerable amount of research has been done on these hypervalent compounds, with a substantial amount of work centered around compounds with phosphorus as the central atom. However, a rather limited amount of attention has been paid to tetravalent ate species containing pnictogen-carbon bonds which can be formulated as 10-Pn-4 compounds. In the case of antimony only several compounds have actually been isolated, and among them the structure of only $[R_2SbX_2]^-$ and $[RSbX_3]^-$ (R=Ph, Me) have been determined by X-ray structural analysis.(2) Herein, we report the preparation, structural determination, and unique reactivity of novel 10-Sb-4 type organoantimony ate complexes **1**.

Compound **1a** was synthesized by the following procedure. To a precooled (-78 °C) THF solution of antimony trichloride (2.0 g, 8.8 mmol) was slowly added a THF solution of two equivalents of dilithiated hexafluorocumyl alcohol (18 mmol), prepared according to the method of Martin et al.(3) The mixture was allowed to warm to room temperature and was stirred overnight. Aqueous workup followed by column chromatographic purification (SiO_2/AcOEt) furnished the lithium salt **1a** (2.2 g, 41%). Treatment of the isolated compound with tetraethylammonium bromide in acetone followed by aqueous workup and recrystallization from acetone-ether gave the corresponding salt **1b** as an anhydrous compound (88%).(4)

Unlike the acyclic ate complexes such as $[R_2SbX_2]^-$ and $[RSbX_3]^-$ (R=Ph, Me), **1** was found to be remarkably stable towards air and water in spite if its anionic character, as shown by its resistance to decompose during the aqueous workup process. This parallels the thermodynamic stability of analogous phosphorus(5) and bismuth(6) compounds that have been established. But in contrast to the phosphorus analog in which protonation gradually occurs on the phosphorus atom upon exposure to atmospheric moisture to yield a 10-P-5 species and the bismuth analog in which protonation occurs on the ligand oxygen atom upon chromatographic treatment to yield an 8-Bi-3 species, **1a, b** maintain their structural integrity.

The room temperature ^{19}F NMR of **1b** showed a pair of quartets [δ -75.8, -73.4 (J=9.3 Hz)(split width ($\Delta\nu$) 204 Hz)] for the anisochronous pair of trifluoromethyl groups. Furthermore variable temperature NMR

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† Dedicated to celebrate the 80th birthday of Dr. Osamu Simamura, Emeritus Professor of The University of Tokyo.

measurements of the compounds showed essentially no change in the band shape of the NMR signals up to 150 °C in DMSO-d_6. This indicates the high configurational rigidity of this compound, although this compound can be regarded formally as a five ligand system (assuming the lone pair as a formal ligand) and thus could be assumed to be susceptible to Berry type pseudorotation.

The X-ray structural analysis of **1b**7) further supports the observations in solution. The ORTEP structure and typical structural values are shown in Fig. 1 and Table 1, respectively, which show that **1b** has a distorted pseudo-trigonal bipyamidal structure with the oxygen atoms in the apical positions. The angle deviations from an ideal trigonal bipyramid are shown in parentheses. Such is caused mainly by the electrostatic repulsion between the lone pair electrons and the covalent bond electrons. O1-Sb-C11=78.1°(11.9° from 90°), O2-Sb-C21=77.5°(12.5° from 90°), O1-Sb-O2=159.3°(20.7° from 180°). C11-Sb-C21=103.6°(16.4° from 120°). The bond lengths of corresponding pairs of bonds, Sb-O1=2.13 Å and Sb-O2=2.14 Å; Sb-C11=2.16 Å and Sb-C21=2.13 Å, are each almost identical, showing the high degree of C_2 symmetry of the ate complex. As preliminary data we have obtained X-ray structural data on an analogous neutral 10-Sb-5 compound with a chlorine in the place of the lone pair, which has a structure closer to ideal TBP structure. Determined bond lengths are Sb-O1=2.014 Å, Sb-O2=2.017 Å, Sb-C11=2.079 Å, Sb-C21=2.075 Å with O1-Sb-O2=176.9°.8) This indicates that compared with this pentacoordinated species the bond lengthening in the anionic species is 5.8%, 6.0%, 3.9%, 2.7%, respectively, showing an appreciable difference in degree of bond lengthening between Sb-O and Sb-C bonds. The cause of the bond lengthening in the apical bonds could be attributed for the most part to the electrostatic repulsion. Thus, although the possibility that this compound is actually in equilibrium with fast exchange between the 10-Sb-4 species and two ring-opened 8-Sb-3 topomers with one Sb-O bond and one free oxygen anion cannot be denied completely, based upon these observations the contribution of the 8-Sb-3 species can be considered to be very small if there is any at all.

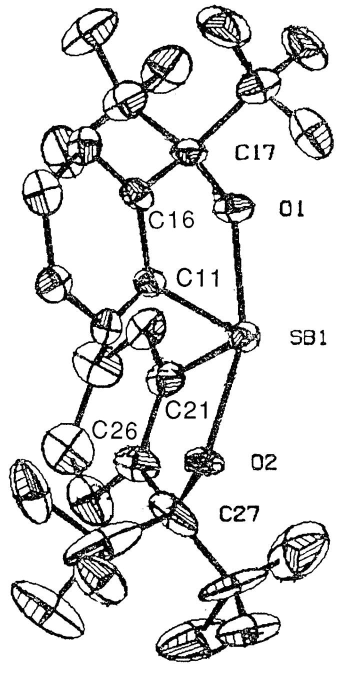


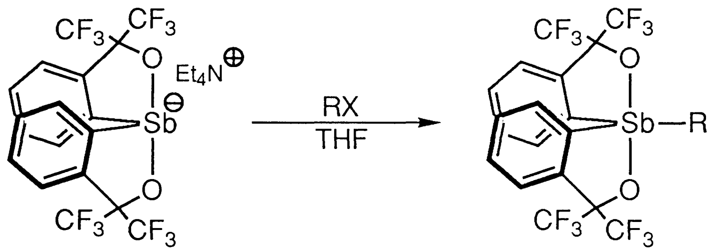
Fig. 1. ORTEP of **1b**.

Table 1. Selected Crystallographic Data (R=0.075)

	Bond length/Å		
Sb-O1	2.13(1)	Sb-O2	2.14(1)
Sb-C11	2.16(2)	Sb-C21	2.13(2)
O1-C17	1.36(2)	O2-C27	1.34(3)
C11-C16	1.40(2)	C21-C26	1.40(2)
C16-C17	1.56(2)	C26-C27	1.58(3)
	Bond angle/deg		
O1-Sb-O2	159.3(4)	C11-Sb-C21	103.6(6)
O1-Sb-C11	78.1(5)	O2-Sb-C21	77.5(5)
O1-C17-C16	115 (1)	O2-C27-C26	113 (2)
Sb-O1-C17	116 (1)	Sb-O2-C27	116 (1)
Sb-C11-C16	115 (1)	Sb-C21-C26	116 (1)
C11-C16-C17	114 (2)	C21-C26-C27	113 (2)

To examine the reactivity of this compound we treated **1b** with various alkyl halides in THF, which normally are not reactive enough to quaternize tertiary triarylantimony compounds.

As shown in Table 1, the reactions took place readily to yield the corresponding neutral 10-Sb-5 type compounds in good yields.[9] In the case of MeI (entry 1), the reaction took place instantaneously after addition of the reagent at room temperature while with other reagents longer reaction time or higher temperatures were required. These products also showed high configurational rigidity on the variable temperature ^{19}F NMR time scale.



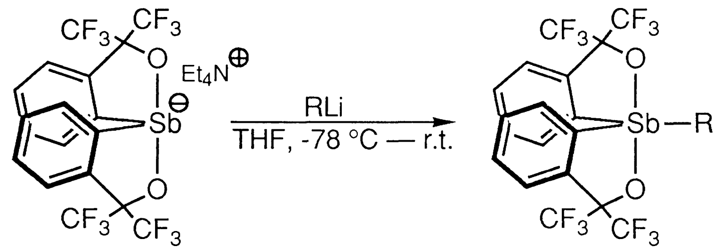
1b **2a-e** (1)

Table 1. Reaction with Alkyl Halides

	RX	Condition	Yield/%
2a	CH_3I	rt	94
2b	$PhCH_2Br$	rt	88
2c	$CH_2=CHCH_2Br$	reflux	91
2d	$CH_3CH_2CH_2CH_2Br$	reflux-NaI[a]	95
2e	$C_2H_5OCOCH_2Br$	rt	94

a) Additive.

Interestingly, the ate complex showed ambiphilic character by also reacting with organolithium reagents to give 10-Sb-5 type pentavalent compounds after workup. The results are listed in Table 2. The fact that a bond was formed between antimony and nucleophilic carbon implies that although the molecule itself is negatively charged, the central antimony atom retains a substantial amount of positive charge.

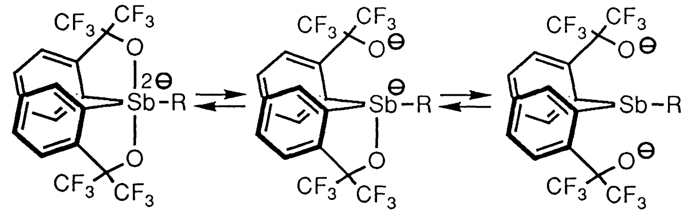


1b **2a,d,f,g** (2)

This phenomenon coincides with predictions from theoretical calculations performed by Trinquier et al. on compounds of phosphorus and arsenic having differing number of ligands.[10] Their results showed the net charge on the central atom in PnH_3, PnH_4^-, PnH_5, PnH_6^- with Pn=P to be +0.21, +0.20, +0.66, +0.68 and with Pn=As to be +0.21, +0.24, +0.68, +0.86, respectively, implying that the addition of an extra anionic ligand does not decrease the positive charge of the central atom regardless of the fact that the electronegativity of hydrogen is not very high. This trend is expected to carry on into the antimony series with even a larger amount of positive charge on the antimony atom in the anionic species. Since our compound has two oxygens in the place of hydrogens along with two carbons that can be regarded to behave similarly to hydrogens, our results are understandable. Thus, the initial addition of the nucleophile probably creates an equilibrium mixture of the three dianionic species as shown in Eq. 3. Since the ultimate product has a Sb(V) center, the Sb(III) center of the dianion is probably air oxidized upon exposure to the atmosphere.

Table 2. Reaction with Lithium Reagents

	RLi	Yield/%
2a	CH_3Li	68
2d	$CH_3CH_2CH_2CH_2Li$	61
2f	$p\text{-}CH_3C_6H_4Li$	51
2g	$p\text{-}CF_3C_6H_4Li$	16



(3)

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4) **1a**: Mp 166-170 °C; ^{1}H NMR (acetone-d_6) δ 7.0-7.5 (m, 6H), 7.9-8.0 (m, 2H); ^{19}F NMR (acetone-d_6) δ -75.7 (q, 6F, J=9.3 Hz), -73.3 (q, 6F, J=9.3 Hz). **1b**: Mp 141-143°C; ^{1}H NMR (acetone-d_6) δ 1.28 (t of t, 12H, J=7.3, 1.7 Hz), 3.37 (q, 8H, J=7.3 Hz), 7.0-7.5 (m, 6H), 7.9-8.0 (m, 2H); ^{19}F NMR (acetone-d_6) δ -75.8 (q, 6F, J=9.3 Hz), -73.4 (q, 6F, J=9.3 Hz); Found: C, 42.49; H, 3.99; N, 1.67%. Calcd for $C_{26}H_{28}F_{12}NO_2Sb$: C, 42.42; H, 3.83; N, 1.90%.

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7) Crystallographic data for **1b**: $C_{26}H_{28}F_{12}NO_2Sb$, FW=736.19, monoclinic, space group $P2_1/n$, a=20.305(2) Å, b=16.931(2) Å, c=9.340(1) Å, β=96.823(9)°, V=3188.4(6) Å^3, Z=4, D_c=1.53 g cm^{-3}, Mo $K\alpha$ radiation, 3415 reflections used, R=0.075, R_w=0.092.

8) Unpublished data.

9) All data were measured with $CDCl_3$ as solvent; **2a**: ^{1}H NMR 1.90 (s, 3H), 7.5-8.0 (m, 6H), 8.0-8.2 (m, 2H), ^{19}F NMR -76.4 (q, 6H, J=7.2 Hz), -76.0 (q, 6H, J=7.2 Hz); **2b**: ^{1}H NMR 3.64 (d, 1H, J=11.3 Hz) 3.77 (d, 1H, J=11.3 Hz), 7.08 (s, 5H), 7.5-8.0 (m, 8H), ^{19}F NMR -76.2 (q, 6H, J=8.3 Hz), -75.5 (q, 6H, J=8.3 Hz); **2c**: ^{1}H NMR 0.88 (t, 3H, J=6.8 Hz), 1.2-2.0 (m, 4H), 2.3-2.7 (m, 2H), 7.5-8.0 (m, 6H), 8.0-8.2 (m, 2H) ^{19}F NMR -76.0 (s, 12H); **2d:** ^{1}H NMR 3.19 (dd, 1H, J=11.5, 8.3 Hz), 3.30 (dd, 1H, J=11.5, 7.7 Hz), 5.12 (dd, 1H, J=10.0, 1.2 Hz), 5.18 (dd, 1H, J=17.1, 1.2 Hz), 5.9 (dddd, 1H, J=17.1, 10,0, 8.3, 7.7 Hz), 7.6-8.0 (m, 6H), 8.0-8.2 (m, 2H), ^{19}F NMR -76.0 (s, 12H); **2e**: ^{1}H NMR 1.08 (t, 3H, J=7.3 Hz), 3.34 (s, 2H), 4.07 (q, 1H, J= 7.3 Hz), 4.09 (q, 1H, J=7.3 Hz), 7.6-8.0 (m, 6H), 8.0-8.2 (m, 2H),.^{19}F NMR -76.0 (s, 12H); **2f**: ^{1}H NMR 2.33 (s, 3H), 7.32 (d, 2H, J=7.9 Hz), 7.5-7.9 (m, 6H), 7.92 (d, 2H, J=7.9 Hz), 8.0-8.2 (m, 2H), ^{19}F NMR -74.2 (q, 6F, J=8.3 Hz), -73.0 (q, 6F, J=8.3 Hz); **2g**: ^{1}H NMR 7.5-7.9 (m, 8H), 8.0-8.3 (m, 8H), ^{19}F NMR -75.9 (q, 6F, J=8.3 Hz),-74.6 (q, 6F, J=8.3 Hz), -63.9 (s, 3F). **2c-f** gave correct elemental analyses.

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