Monomeric 10-Sb-5 Pentacoordinate Organoantimony Monohalides and Their Permutational Behavior

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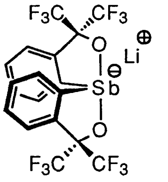
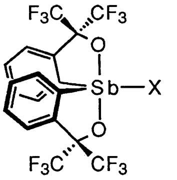
Pentacoordinate organoantimony monohalides [*o*-$O(CF_3)_2C_6H_4]_2SbX$ (X=F, Cl, Br, I) were found to topologically permutate intramolecularly as monomers with energy barriers in the order of F < Cl < Br < I in toluene and Br < Cl < I < F in THF.

Since the antimony-element bonds are weaker than those of congener elements such as phosphorus, the permutation barrier naturally becomes smaller and more difficult to observe for pentacoordinate antimony compounds.[1] In addition, due to its metallic nature pentacoordinate antimony exhibits Lewis acid properties and compounds having three or more electronegative heteroatoms usually exist and behave as dimers or higher oligomers in both the solid and solution state.[2] For these reasons there is no reliable evidence on permutation for monomeric antimony compounds in solution[3] as compared with the large amount accumulated for phosphorus.[4] However, by incorporating Martin's bidentate ligands we have for the first time successfully obtained pentacoordinate organoantimony monohalides which bear equatorial halogens and also show monomeric character both in the solid and in solution states. Herein, we describe the results of our findings.

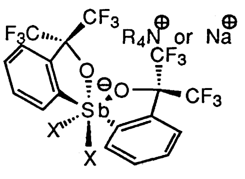
The treatment of a CH_2Cl_2 suspension of **1**-Li^+, which we have found to be a unique water stable 10-Sb-4 species,[5] with sulfuryl chloride, bromine, and iodine each yielded the corresponding 10-Sb-5 halides **2b**, **2c**, and **2d**, quantitatively.[6]



1-Li^+



2a (X=F), **2b** (X=Cl), **2c** (X=Br), **2d** (X=I)



3a (X=F), **3b** (X=Cl), **3c** (X=Br), **3d** (X=I)

Unlike **1**, these monohalides were unstable to aqueous treatment. The ambient temperature ^{19}F NMR spectrum showed a pair of broad singlets, instead of a pair of sharp quartets usually seen for the anisochronous pairs of trifluoromethyl groups of spiropentacoordinate compounds possessing these bidentates, indicative of the presence of some sort of low barrier exchange process. When the halogenation reactions were carried out with **1**-R_4N^+ (R=Et, n-Bu) instead of the lithium salts, the products turned out to be hexacoordinate dihalides **3b**, **3c**, **3d**[6] thus indicating that an equilibrium between the pentacoordinate species and the hexacoordinate species exists in solution with the equilibrium highly favoring the hexacoordinate species. Compound **3a**[6] was prepared by treating **2b** with the appropriate fluoride. All attempts to prepare the pentacoordinate fluoride **2a** in isolated form have met with failure.

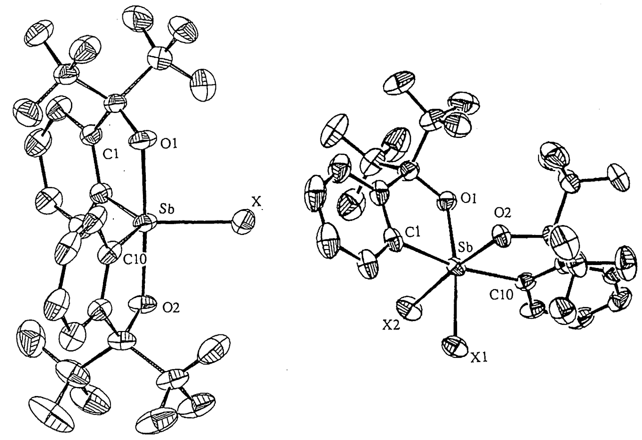


Figure 1. ORTEP drawing of **2b** and **3b**-Bu_4N^+. All hydrogen atoms and Bu_4N^+ of **3b**-Bu_4N^+ have been omitted for clarity.

Table 1. Selected Crystallographic Data for **2b** and **3b**

	2b (X=Cl)	**3b** (X=Cl)
	Bond length/Å	
Sb-O1	2.015(2)	2.043(2)
Sb-O2	2.016(2)	2.035(2)
Sb-C1	2.073(2)	2.114(3)
Sb-C10	2.080(3)	2.105(3)
Sb-Cl1	2.290(1)	2.441(1)
Sb-Cl2	-	2.4591(9)
	Bond angle/deg	
O1-Sb-Cl1	91.70(7)	173.79(6)
O2-Sb-Cl2	-	172.37(7)
C1-Sb-C10	127.0(1)	168.8(2)
C1-Sb-Cl	115.16(8)	93.5(1)
C10-Sb-Cl	117.78(8)	96.2(1)
O1-Sb-C1	82.50(9)	80.5(1)
O2-Sb-C10	82.4(1)	81.0(1)
O1-Sb-O2	177.03(9)	93.02(9)
Cl1-Sb-Cl2	-	87.43(4)

X-ray structural analysis was carried out on pentacoordinate compounds **2b**, **2c**, and **2d**, and hexacoordinate compounds **3a**-Et_4N^+, **3b**-Bu_4N^+, and **3d**-Et_4N^+. The ORTEP drawings of **2b** and **3b**-Bu_4N^+ are shown in Figure 1 (X=Cl) with selected structural parameters of the two in Table 1. The structures of **2c**, **2d**, **3a**, and **3d** were found to have the same configuration as their chlorine analogs. The pentacoordinate group of compounds all adopt slightly distorted trigonal bipyramidal structures with the two oxygen atoms occupying the apical positions, and the remaining halogen and two carbon atoms in the equatorial positions. A remarkable characteristic of these compounds is that the shortest intermolecular Sb-X distance is longer than 5 Å, well longer than the sum of van der Waals radii of 3.95 Å (Sb 2.2 Å, Cl 1.75 Å) for **2b**, 4.05 Å (Sb 2.2 Å, Br 1.85 Å) for **2c**, and 4.18 Å (Sb 2.2 Å, I 1.98 Å)[7] for **2d**, thus showing their essentially monomeric character in the solid state. The solid state structures of the hexacoordinate compounds were all found to have the oxygen and halogen atoms positioned anti with all the bonds about the antimony atom elongated compared with their pentacoordinate counterparts.[8]

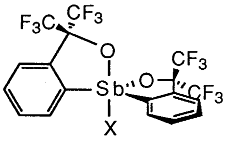
The fact that the halides **2b-d** were monomeric allowed systematical investigation of the intramolecular exchange process of pentacoordinate compounds differing only in the halogen substituent. Variable temperature ^{19}F NMR measurements using non-nucleophilic toluene ($E_T{}^N$=0.099, DN^N=ca. 0) and weakly basic THF ($E_T{}^N$=0.207, DN^N=0.52) as solvent were carried out. The estimated activation energy using the coalescence temperature method are listed in Table 2. The pentacoordinate fluorine compound **2a** was generated in situ by adding a large excess of strong Lewis acids such as SbF_5 or BF_3 etherate to **3a**-M^+ (M^+=Na^+ or K^+). None of the compounds showed notable changes in activation energies in toluene and THF even when the concentration was increased by a factor of about 5; therefore assuring that the elucidated values are of a unimolecular process dealing with intramolecular isomerization. We also found that there was essentially no influence of additives such as **3** on the barrier of **2**, in contrast with results obtained on compounds having a carbon substituent in the place of the halogens.[9] This is probably due to the low barrier for the isomerization of these monohalides as a whole, i. e., the intramolecular permutation is much faster than intermolecular halogen exchange. No observations could be made by variable temperature NMR that could be attributed to intramolecular permutation processes of the hexacoordinate compounds. The order of the activation energies in toluene, F ($\Delta G^{\neq}_{Tc}$=12.8 kcal mol^{-1}) < Cl (14.1) < Br (15.1) < I (16.8), shows that the more electronegative element possesses a lower barrier, a result that indicates that the order of the electronegativities of these elements correlates nicely with the apicophilicity of these elements, F > Cl > Br > I. That is, high energy structures such as **4** which are inevitable on the Berry pseudorotation coordinate are expected to be more stabilized with more electronegative elements in the apical position.

On the other hand, the order of the energy barriers calculated from measurements in THF showed an irregular trend, Br ($\Delta G^{\neq}_{Tc}$=13.4 kcal mol^{-1}) < Cl (14.1) < I (14.3) < F (15.6). The stabilization of the transition state should be in effect as previously reported in the form of ring strain relieved by the interaction of the donor property of the solvent with the antimony atom to give a hexacoordinate transition state such as **5**.[9] Since the atom anti to the nucleophile is the same oxygen for all four compounds the extent of stabilization should be about the same for the four. The fact that hexacoordinate compounds such as **3** with a configuration analogous to **5** can easily be obtained should support this assumption although THF is neutral and has only weak nucleophilicity. Thus the reason for the unordinary order must be the presence of weak stabilization of the ground state structure by the solvent as in **6** and that the overall activation barrier is a balance between the extent of stabilization in the transition and ground states. Since the interaction of the solvent from the back side of the halogen atom is expected to be the factor of stabilization in the ground state structure, it would be natural that the more electronegative halogen would allow a stronger interaction of the solvent and thus larger stabilization of the ground state. Therefore, there is no surprise that the fluorine compound **2a** has the largest barrier in THF.

Table 2. Activation Energy of Permutation of **2a-d**[a]

	toluene			THF		
X	$\Delta\nu^b$ (Hz)	Tc^c (K)	$\Delta G^{\neq}_{Tc}$ (kcal mol^{-1})	$\Delta\nu^b$ (Hz)	Tc^c (K)	$\Delta G^{\neq}_{Tc}$ (kcal mol^{-1})
F	247	278	12.8	246	338	15.6
Cl	410	313	14.1	185	303	14.1
Br	470	336	15.1	385	298	13.4
I	121*	351	16.8	759	325	14.3

[a]Measured at 376 MHz. (* Measured at 85 MHz). [b]Split width of CF_3 groups. [c]Coalescence temperature.



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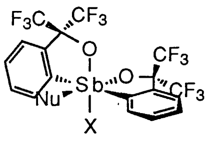

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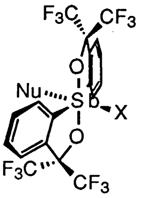

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In summary, we have systematically determined the permutation barrier for monomeric 10-Sb-5 organoantimony compounds bearing equatorial halogen substituents. It was found that the more electronegative halogen accelerates the pseudorotation in toluene while a considerable solvent effect is present in THF.

References and Notes

1 For example: D. Hellwinkel and W. Lindner, *Chem. Ber.*, **109**, 1497 (1976).

2 For example: W. Schwarz and H.-J. Guder, *Z. Naturforsch.*, **33B**, 485 (1978); J. Bordner, G. O. Doak, and J. R. Peters, Jr., *J. Am. Chem. Soc.*, **96**, 6763 (1974).

3 For pentahalogen compounds in the gas phase: L. S. Ivashkevich, A. A. Ishchenko, V. P. Spiridonov, T. G. Strand, A. A. Ivanov, and A. N. Nikolaev, *Russ. J. Struct. Chem.*, **23**, 295 (1982).

4 For example: R. R. Holmes, "Pentacoordinated Phosphorus," ACS Monograph Series 175 and 176, American Chemical Society, Washington, DC (1980), Vols 1 and 2.

5 K.-y. Akiba, H. Nakata, Y. Yamamoto, and S. Kojima, *Chem. Lett.*, **1992**, 1559.

6 All compounds gave correct elemental analysis and reasonable spectra. Mp: **2b** 145-146 °C; **2c** 150-151 °C; **2d** 278-279 °C; **3a**-Et_4N^+ 230-231 °C; **3b**-Et_4N^+ 270-272 °C; **3b**-Bu_4N^+ 187-188 °C; **3c**-Et_4N^+ 262-264 °C; **3d**-Et_4N^+ 224-226 °C.

7 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

8 Detailed comparison of solid state structures of **2** and **3** will be published elsewhere. Crystallographic data for **2b**: $C_{18}H_8ClF_{12}O_2Sb$, FW=641.40, monoclinic, space group $A2/a$, a=23.434(9) Å, b=8.212(4) Å, c=22.248(8) Å, β=99.19(3)°, V=4226(3) Å^3, Z=8, D_c=2.02 g cm^{-3}, Mo $K\alpha$ radiation, 4406 reflections used, R=0.030, Rw=0.031. Crystallographic data for **3b**-Bu_4N^+: $C_{34}H_{44}Cl_2F_{12}NO_2Sb$, FW=919.40, triclinic, space group $P\bar{1}$, a=10.664(2) Å, b=11.710(5) Å, c=16.443(3) Å, α=85.89(2)°, β=75.71(1)°, χ=85.80(2)°, V=1981.2(9) Å^3, Z=2, D_c=1.54 g cm^{-3}, Mo $K\alpha$ radiation, 6160 reflections used, R=0.035, Rw=0.026.

9 S. Kojima, Y. Doi, M. Okuda, and K. -y. Akiba, *Organometallics*, **14**, 1928 (1995).