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Pentacoordinate Organoantimony Compounds That Isomerize by Turnstile Rotation

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The fluxional behavior of pentacoordinate group 15 element compounds such as phosphoranes, which generally assume a trigonal bipyramidal (TBP) geometry, have been widely investigated for over four decades in relation to their biological activities.[1,2] The most accepted mechanism for the stereomutation of such species is called "Berry pseudorotation (BPR)",[3] which is frequently used to describe the intramolecular ligand exchange of TBP-shaped molecules (Figure 1). An alternative mechanism which is occasionally taken into account is "turnstile rotation (TR)" proposed by Ramirez and Ugi.[4]

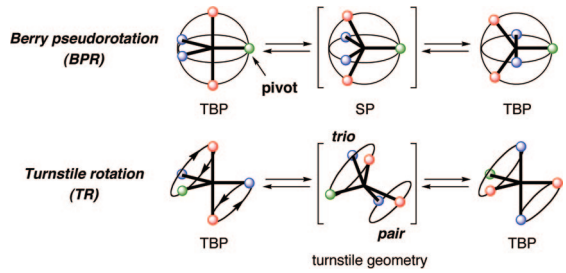


Figure 1. Schematic representation of the mechanism of BPR and TR.

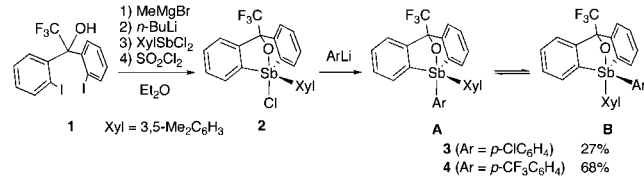
The mechanism of TR can be expressed as a relative internal rotation of a *trio* (a set of an apical and two equatorial ligands) versus *pair* (a set of an apical and an equatorial ligand), whereas BPR involves only simple bending motions. A limited number of theoretical studies have demonstrated that BPR is a favorable process for the stereomutation of hypervalent compounds. Although quite rapid stereomutations of some phosphoranes having the rigid tridentate ligand may be explained by TR rather than BPR,[5] TR is considered to be higher in energy than BPR or not a process with a distinct physical reality in the chemistry of pentacoordinate main group elements.[6]

Because TR and BPR give the same stereomutational result, it is impossible to distinguish between the two mechanisms by analyzing the products. However, if only the BPR process can be completely frozen by introduction of a well-designed rigid tridentate ligand occupying an apical and two equatorial sites of a TBP structure, stereomutation should be originated by the TR process because the tridentate ligand can freeze only BPR and exclusively function as a *trio* during TR (Figure 1).

Here we report the isolation and characterization of two stereoisomers of pentacoordinate antimony compounds (stiboranes) using a newly developed tridentate ligand, stereomutation between the two stereoisomers, and evaluation of the stereomutation mechanism by a computational study.

A precursor of the new rigid tridentate ligand, i.e., 1,1-bis(2-iodophenyl)-2,2,2-trifluoroethanol (**1**), was prepared from aniline in 55% total yield (4 steps, see Supporting Information). Alcohol **1** was successfully trimetallated by treatment with 1 equiv of MeMgBr followed by 3 equiv of *n*-BuLi in Et_2O. A chlorostiborane bearing the tridentate ligand (**2**) was then prepared in 52% yield as a single isomer by the reaction of trimetallated **1** with $XylSbCl_2$ (Xyl = 3,5-$Me_2C_6H_3$), followed by oxidative chlorination using SO_2Cl_2 (Scheme 1, see Supporting Information for X-ray analysis of **2**).

Scheme 1



Reactions of **2** with ArLi (Ar = *p*-ClC_6H_4 and *p*-$CF_3C_6H_4$) afforded the corresponding stiboranes bearing two aryl monodentate ligands (**3** and **4**) in 27% and 68% yield, respectively. Compounds **3** and **4** were given as a mixture of two stereoisomers **A** and **B**. For both **3** and **4**, the ^1H NMR ($CDCl_3$) showed two singlets for the *ortho*-protons of the Xyl group (**3**: δ 7.58 (major) and 7.04 (minor); ratio 74:26; **4**: δ 7.57 (major) and 7.03 (minor); ratio 70:30). The major signals were assigned to isomer **A** (Xyl-equatorial) from the signals of pure **3A** and **4A**, which were obtained as crystals (vide infra); thus the minor signals were assigned to isomer **B** (Xyl-apical).

Single crystals of stereoisomers **3A** and **4A** were obtained by recrystallization of the corresponding mixture of **A** and **B** from Et_2O/*n*-hexane at rt. Note that recrystallization of the mixture of **3A** and **3B** from CH_3CN at −17 °C afforded single crystals of **3B** (thin plate) along with those of **3A** (prism).

The solid state structure of **3A**, **3B**, and **4A** was confirmed by X-ray crystallographic analysis. The ORTEP drawings for the two stereoisomers of **3** are shown in Figure 2 (for **4A**, see Supporting Information). The structures are slightly distorted TBP geometries with the apical bond angles (ca. 175°) close to an ideal 180°. The Sb1−C3 distances are longer than the Sb1−C4 distances for all compounds by 0.04−0.06 Å, indicating that the two aryl monodentate groups of **3A**, **3B**, and **4A** are located at an equatorial and an apical site. These structures are in good agreement with the solution structures predicted by the NMR analyses.

When pure isomer **A** (**3A** or **4A**) was dissolved in dry toluene-d_8, isomerization slowly occurred to afford an equilibrated mixture of **A** and **B** (**3A** and **3B** or **4A** and **4B**) at elevated (>40 °C) temperatures. Unfortunately, the *p*-chlorophenyl derivative (**3**) was not suitable for kinetic measurements of the isomerization because

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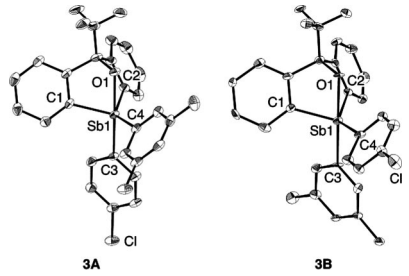


Figure 2. ORTEP drawings of **3A** and **3B** with the thermal ellipsoids shown at the 30% probability level with hydrogen atoms omitted for clarity. For **3B**, one of the two independent molecules is shown.

the ^{1}H NMR signals of **3A** and **3B** were not well resolved, although the structures of both stereoisomers were unveiled. Therefore, kinetic measurements were performed using **4**, and the reaction was monitored by the ^{19}F NMR signal of the *p*-CF_3 group over the temperature range 80−100 °C. The isomerization proceeded with reversible first-order kinetics. The activation parameters obtained from the Eyring plot are as follows: (**4A** to **4B**) $\Delta H^{\ddagger} = 28.9 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = 1.3 \pm 2.5$ e.u., $\Delta G^{\ddagger}_{298} = 28.6$ kcal mol^{-1}; (**4B** to **4A**) $\Delta H^{\ddagger} = 28.2 \pm 0.9$ kcal mol^{-1}, $\Delta S^{\ddagger} = 0.9 \pm 2.3$ e.u., $\Delta G^{\ddagger}_{298} = 27.9$ kcal mol^{-1}. Since the activation enthropies are virtually zero, the stereomutation between **4A** and **4B** should be an intramolecular process.

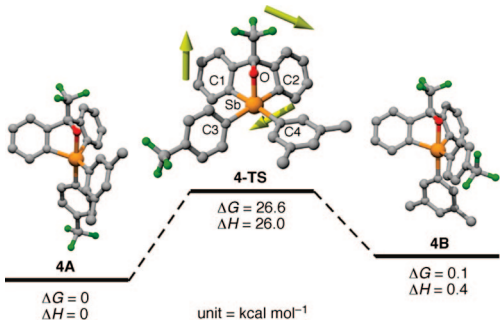
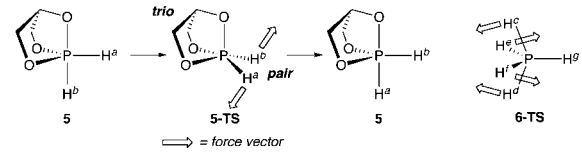


Figure 3. Calculated energies for the isomerization between **4A** and **4B**. Yellow arrows denote the motions of substituents in **4-TS** determined by force vectors of each atom.

To better understand the stereomutation process, the reaction mechanism was studied computationally. The calculations were performed by the B3LYP hybrid functional together with the 6−31G* (Sb: LANL2DZ*) basis set. Starting from the transition state structure (**4-TS**), the reaction path was followed by IRC analysis (Figure 3). The calculated structure of **4A** was in good agreement with the crystal structure. The activation free energies of the stereomutation were 26.6 (**4A** to **4B**) and 26.5 (**4B** to **4A**) kcal mol^{-1}. These values were also in good agreement with the experimental data. In the structure of transition state **4-TS**, the small O−Sb−C1 (80.33°) and O−Sb−C2 (81.30°) angles and the large C1−Sb−C4 (173.90°) and C2−Sb−C3 (166.49°) angles were departed from ideal angles for the SP structure (103° and 154°), which is a transition state in the BPR process.

A distinct difference between TR and BPR can be given by the force vector of each atom in the transition state.[7] For **4-TS**, the force vectors indicate the rotation of the tridentate ligand (yellow arrows in Figure 3), and this motion is essentially consistent with the motion of the TR process.[8] Although only the motion of a *trio* was apparently observed, this is the result of a relative rotation of a *trio* and *pair* in the TR process. Actually, for a model phosphorane with a rigid tridentate ligand (**5**), the force vectors in **5-TS** show the motion of a *pair* (H^a and H^b) probably because lighter hydrogen atoms move easier than the heavier tridentate ligand, indicating also the relative rotation of a *trio* and *pair* in the TR process (Scheme 2). Another model phosphorane PH_5 (**6**) was calculated for comparison. The direction of force vectors in **6-TS** is completely different from that of vectors in **4-TS** and in **5-TS**, showing that the force vectors of two apical hydrogen atoms (H^c and H^d) are opposite to those of two equatorial hydrogen atoms (H^e and H^f), which is in good agreement with ideal BPR motion.

Scheme 2



In conclusion, we isolated two stereoisomers of stiboranes **3** and **4** with a rigid tridentate ligand, and the isomerization of **4** was found to proceed by the TR mechanism with the tridentate ligand as a *trio* and the two monodentate ligands as a *pair*.[9]

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Supporting Information Available: Full experimental procedures, spectroscopic, crystallographic (CIF) data, and the *xyz* coordinates for the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The mechanism of the stereomutation of **4** is classified to Muetterties' mechanism 2 giving the same result of the 3-fold TR (= $(TR)^3$). For the Muetterties' mechanisms for pentacoodinated molecules, see: Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 4115–4122. For the $(TR)^3$, see ref 4.
(9) We found that donor solvents accelerated the isomerization of **4**, where the isomerization rate was correlated with the donor number of solvents, not with polarity parameters (e.g., dielectric constant). Thus, another mechanism involving edge inversion of tetrahedral ionic species after cleavage of the Sb−O bond of **4** should be ruled out. The results will be submitted elsewhere.

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