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Supplementary Material Available: X-ray crystallographic data for 4-carboxyphenyl azide, including tables of positional and thermal parameters, bond distances, and bond angles (4 pages); table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

Synthesis and Crystal Structure of Intramolecularly Coordinated Organobismuth Compounds and Edge Inversion at Trivalent Bismuth

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Inversion at the central atom has been recognized to be a slow process among group 15 elements[1] except the classical vertex inversion of nitrogen (6 kcal mol^{-1} for NH_3).[2] The vertex inversion barriers typified by PnH_3 (Pn = pnictogen) have been calculated to increase with increasing pnictogen atomic number.[3] On the other hand, edge inversion, recently proposed by Arduengo and Dixon, predicts the following: (1) inversion barrier decreases with increasing pnictogen atomic number, (2) σ-acceptors (electronegative substituents) stabilize the T-shaped transition state, and (3) coordination of an empty p-orbital appearing at the transition state with nucleophiles also stabilizes the transition state.[3,4] Hence, trivalent organobismuth compounds should be suitable to test for edge inversion. Although only a few papers concerning inversion at trivalent bismuth have been reported, none of them have estimated the barriers of inversion.[5] We report here a unique example of edge inversion.

1-(*p*-Methylphenyl)-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxabismole (**1**)[6] was prepared from dichloro(*p*-methylphenyl)bismuth and dilithio reagent **2a**.[7] The ^{19}F NMR spectrum (acetone-d_6) of **1** shows a pair of quartets [δ −75.7, −78.3 (J = 8.7 Hz) (split width ($\Delta\nu$) 220 Hz)] for the CF_3 groups at room temperature,

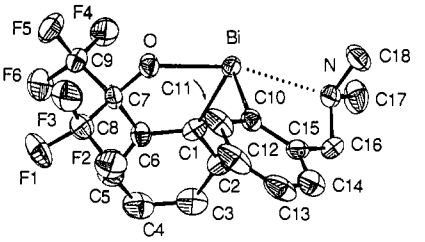
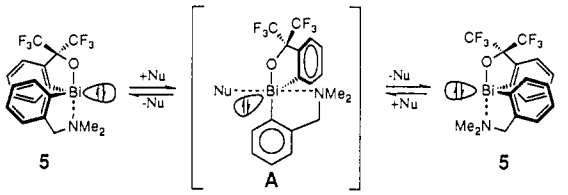


Figure 1. An ORTEP drawing of **5**.

Table I. Coalescence Temperatures (T_c) and Free Energies of Activation ($\Delta G^{\ddagger}_{Tc}$) in DMSO-d_6

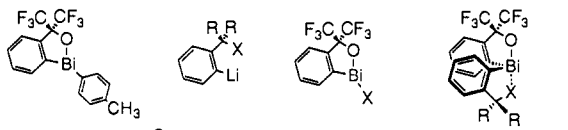
	compounds		
	1	**4**	**5**
T_c (°C)	175	125	55
$\Delta G^{\ddagger}_{Tc}$ (kcal mol^{-1})	21.2 ± 0.1	18.6 ± 0.1	15.4 ± 0.1

Scheme I. Nucleophilic Stabilization by the Intramolecular Substituent (NMe_2) and the Solvent (Nu: Pyridine in this case) for the Intermediate A in the Edge Inversion



demonstrating that the compound possesses a stable pyramidal configuration. At 175 °C in DMSO-d_6, coalescence of the two CF_3 groups was observed, and the energy for the inversion was calculated to be 21.2 kcal mol^{-1} (175 °C). Coalescence was not observed in *o*-dichlorobenzene and benzonitrile until 175 °C.

Surprisingly, ^{19}F NMR spectra (acetone-d_6) of **3** bearing electronegative substituents such as chlorine (**3a**),[8] acetoxy (**3b**),[8] and trifluoroacetoxy (**3c**)[8] groups show a singlet even at −50 °C. Hence, the inversion is much faster in **3** than in **1**. In contrast, the vertex inversion barrier of Me_2PCl (40.4 kcal mol^{-1}) is known to be higher than that of Me_3P (35.6 kcal mol^{-1}).[9] Thus, the result suggests that the inversion takes place via edge inversion. However, there is a possibility of inversion by an intermolecular process for **3** and also a possibility of an intramolecular process via a four-membered cyclic transition state by coordination of the carbonyl oxygen to the bismuth. Therefore, in order to investigate the possibility of an edge inversion process, we synthesized **4**[10] and **5**[11] by the reaction of **2b** or **2c** with **3a**.



1 **2a**: R=CF_3; X=OLi **3a**: X=Cl **4**: R=CH_3; X=OMe
2b: R=CH_3; X=OMe **3b**: X=CH_3CO_2 **5**: R=H; X=NMe_2
2c: R=H; X=NMe_2 **3c**: X=CF_3CO_2

The structures of **4** and **5** were shown to be quite similar by X-ray crystallography, and an ORTEP diagram of **5** is shown in Figure 1.[12] The distance between the nitrogen of the *N,N*-di-

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(6) **1**: mp >300 °C; ^1H NMR (acetone-d_6) δ 2.24 (s, 3 H), 7.35 (d, J = 7.5 Hz, 2 H), 8.03 (d, J = 7.5 Hz, 2 H), 7.30–8.08 (m, 4 H); ^{19}F NMR (acetone-d_6) δ −75.7 (q, J = 8.7 Hz, 3 F), −78.3 (q, J = 8.7 Hz, 3 F). All of the important compounds gave correct elemental analyses: **1**, **3b**, **3c**, **4**, **5**, and **7**.
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(8) **3a**: mp ca. 130 °C dec; **3a** was almost pure but did not give the correct elemental analysis. **3b**: mp 267–269 °C dec. **3c**: mp 185–186 °C.
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(10) **4**: mp 234–235 °C; ^1H NMR ($CDCl_3$) δ 1.56–1.63 (m, 6 H), 3.80 (s, 3 H), 7.10–7.90 (m, 7 H), 8.10–8.20 (m, 1 H); ^{19}F NMR ($CDCl_3$) δ −72.6 (q, J = 8.6 Hz, 3 F), −75.9 (q, J = 8.6 Hz, 3 F).
(11) **5**: mp 194–195 °C; ^1H NMR (acetone-d_6) δ 2.75 (s, 6 H), 4.04 (d, J = 15 Hz, 1 H), 4.09 (d, J = 15 Hz, 1 H), 7.23–7.29 (m, 6 H), 8.00 (ddd, J = 7.3, 0.7, 0.4 Hz, 1 H), 8.22 (dd, J = 7.3, 1.1 Hz, 1 H); ^{19}F NMR (acetone-d_6) δ −73.1 (q, J = 8.3 Hz, 3 F), −76.5 (q, J = 8.3 Hz, 3 F).

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Table II. Coalescence Temperatures (T_c) and Free Energies of Activation ($\Delta G^{\ddagger}_{Tc}$) of **5**

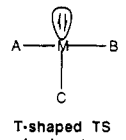
	solvents				
	toluene-d_8[a]	nitrobenzene	2,6-lutidine	DMSO-d_6	pyridine
T_c (°C)	125	170	170	55	40
$\Delta G^{\ddagger}_{Tc}$ (kcal mol^{-1})	20.5 ± 0.1	20.6 ± 0.1	20.6 ± 0.1	15.4 ± 0.1	14.6 ± 0.1

[a] Coalescence could be observed only for CH_2 group.

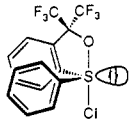
methylamino group and the central bismuth atom is 2.63 Å, which is very much shorter than the sum of van der Waals radii (ca. 3.74 Å).[13] Thus, the coordination of the NMe_2 group effectively forms a hypervalent 10-Bi-4[14] compound. The geometry about the bismuth atom is a distorted pseudotrigonal bipyramid, where the carbon atoms bound to bismuth occupy the equatorial plane with a C-Bi-C angle of 93.1°. The apical positions are occupied by the oxygen and the nitrogen atoms with an O-Bi-N angle of 160.2°. The apical Bi-O bond length is 2.19 Å. The lone pair of electrons can be considered to occupy one equatorial position.

The ^{19}F NMR peaks (acetone-d_6) of **4** and **5** appear as a pair of quartets [δ -72.6, -75.9 (**4**) (J = 8.6 Hz, $\Delta\nu$ 279 Hz), -73.1, -76.5 (**5**) (J = 8.3 Hz, $\Delta\nu$ 288 Hz)] at room temperature, showing that these compounds also possess stable configurations. At elevated temperatures, these pairs of quartets of **1**, **4**, and **5** coalesce at different temperatures in DMSO-d_6 (Table I). The lowered coalescence temperatures and activation energies ($\Delta G^{\ddagger}_{Tc}$) of compounds **4** and **5** clearly show the distinct effect of intramolecularly coordinating groups (OMe, NMe_2) as compared to noncoordinated **1**.

Solvent effects on the barriers of **5** have been investigated (Table II).[4d,15] The dramatic difference between pyridine and 2,6-lutidine strongly indicates that nucleophilic solvents stabilize the transition state **A** in addition to the NMe_2 substituent as shown in Scheme I. The fact that the inversion of **1** cannot be observed without nucleophilic solvents such as DMSO-d_6 (T_c = 175 °C) and pyridine (T_c = 110 °C) also supports nucleophilic assistance. The barrier of 20.5 kcal mol^{-1} (125 °C) for **5** in toluene-d_8 should be that of an intramolecular edge inversion of **5** without solvent participation since a concentration effect could not be observed at all between 0.14 and 0.017 M. It is thus estimated that the T-shaped transition state is stabilized by at least 5.8 kcal mol^{-1} from intramolecular coordination of the NMe_2 group and by 5.9 kcal mol^{-1} from additional coordination with the solvent pyridine. It should be noted here that the inversion cannot be rationalized by Berry pseudorotation because the lone pair electrons must be placed at an apical position in the inevitable intermediate during the pseudorotation process. The high energy required for such a pseudorotation has been previously demonstrated by the isolation of the chiral 10-S-4 sulfurane **6**.[16]



T-shaped TS of edge inversion



6

7

We have also prepared the corresponding antimony compound **7**.[17] The coalescence of the two CF_3 groups could not be observed, and the inversion barrier was measured to be higher than 20 kcal mol^{-1} (at 150 °C in DMSO-d_6). This is consistent with the prediction by edge inversion.

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Supplementary Material Available: Listings of synthetic procedures of **1**, **3**, **4**, and **5**, tables including activation entropies and activation enthalpies, and a list of the X-ray crystallographic data (intramolecular bond lengths, bond angles, selected intermolecular bond lengths, and positional and thermal parameters) of **4** and **5** (24 pages). Ordering information is given on any current masthead page.

(12) The crystal data for **5** are as follows: $C_{18}H_{16}F_6NOBi$, monoclinic, space group $P2_1/a$, a = 11.050 (2) Å, b = 18.572 (3) Å, c = 9.856 (2) Å, β = 108.21 (1)°, Z = 4. With 3588 reflections of intensity greater than 3σ, the structure was solved by direct methods (Multan 78) and standard difference Fourier techniques. The final R factors were R = 0.062 and R_w = 0.085. The crystal data and the selected bond lengths and bond angles of **4** are as follows: $C_{19}H_{17}F_6O_2Bi$, monoclinic, space group $P2_1/n$, a = 17.807 (4) Å, b = 11.002 (3) Å, c = 10.423 (2) Å, β = 106.68 (2)°, Z = 4, R = 0.059, R_w = 0.074, Bi-O(Me) 2.527 (8) Å, Bi-O(ring) 2.195 (7) Å, ∠O-Bi-O 155.4 (3)°, equatorial ∠C-Bi-C 94.4 (4)°.

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(17) Unpublished result by Doi, Y.; Kojima, S.; Akiba, K.-y. **7**: mp 164-166 °C.

(18) This paper is dedicated to celebrate the 70th birthday of Professor Harold Hart of Michigan State University.

Ferricytochrome *c* Binding Induces Detectable Proton NMR Shift Changes in Cytochrome *c* Peroxidase-CN

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The formation of protein-protein docking complexes involved in electron transfer is currently an intense area of interest that has raised questions about molecular recognition, communication between partner proteins, and association of conformational changes (i.e., conformational gating) with electron-transfer dynamics. One paradigm for studying complex formation between heme redox proteins is the noncovalent complex formed between yeast cytochrome *c* peroxidase (EC 1.1.11.5; CcP) and cytochromes *c* from various species.[1-9]

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