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FIRST EXAMPLE OF THERMALLY STABLE HYPERVALENT BISMUTH ATE COMPLEX (12-Bi-6) WITH TWO BIDENTATE LIGANDS: SYNTHESIS AND STRUCTURE

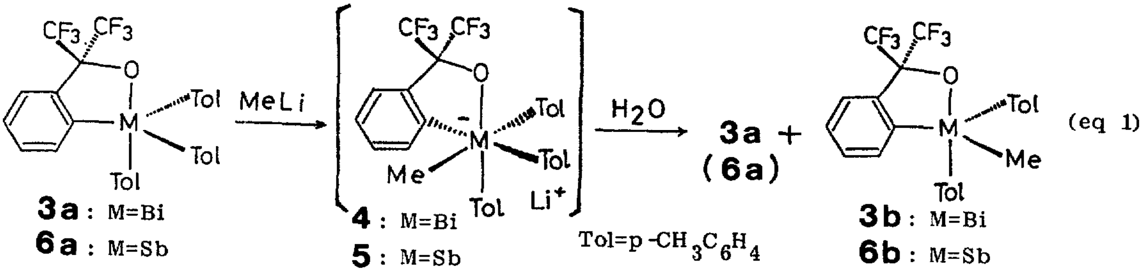
Kin-ya Akiba,* Keisuke Ohdoi, and Yohsuke Yamamoto
Department of Chemistry, Faculty of Science, Hiroshima University,
Higashisenda-machi, Naka-ku, Hiroshima 730, JAPAN

Abstract: A remarkably stable hexacoordinate bismuth ate complex (**1A**) with two bidentate ligands was synthesized by the reaction of a pentacoordinate bismuth compound bearing a Bi-Cl bond (**7**) with a dilithiated reagent (**2**). The complex was stable up to 150 °C and was decomposed by water to afford an alcohol (**11**) quantitatively.

Hypervalent bismuth compounds are generally of low stability because of the weakness of Bi-C bonds.[1] In fact, the number of isolated pentacoordinate bismuth compounds (10-Bi-5) was much less than that of 10-Sb-5.[2] In addition, hexacoordinate bismuth ate complexes (12-Bi-6) have only been obtained as unstable solids in the reactions of pentaphenylbismuth or 2,2'-biphenylene-triphenylbismole with phenyllithium.[3,4] These ate complexes were reported to be stable only at low temperatures and the spectral evidence for the complexes has not been given at all. Here we report the first spectral evidence for a remarkably stable 12-Bi-6 ate complex (**1A**) by use of two bidentate ligands (**2**).

Reaction of 1 equiv of methyllithium with 1,1,1-tris(p-methylphenyl)-3,3-bis(trifluoromethyl)-3H-2,1-benzoxabismole (**3a**)[5] was carried out at 0 °C and the mixture was quenched with water after stirring for 1.5 h at room temperature (eq 1). Pentacoordinate compounds **3a** and **3b** were obtained in good yield (10 and 70 %, respectively) by TLC (SiO_2; ethyl acetate:n-hexane=1:9) but only 20 % of **3a** was recovered after stirring the mixture for 1 day. The result indicated that **4** gradually decomposed at room temperature. The instability of **4** was a contrast to the stability of the corresponding 12-Sb-6 (5), which gave **6a** and **6b** (5:95) in 97 % yield even after stirring for 1 day at room temperature.[6]

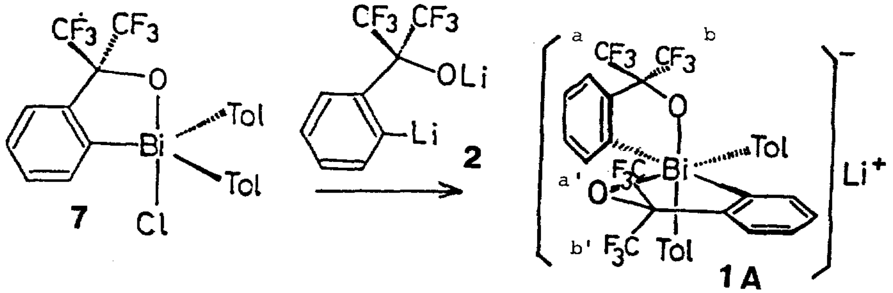
In order to stabilze a 12-Bi-6 compound, we tried to combine two



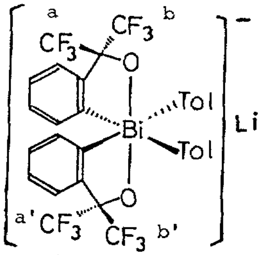
(eq 1)

Tol=p-$CH_3C_6H_4$

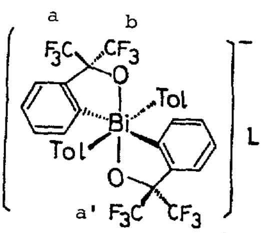
bidentate ligands for the ate complex (1) by the reaction of a 10-Bi-5 compound (7) bearing a Bi-Cl bond[5] with the dilithiated reagent (2) (eq 2).[7] The compound 2 prepared from bis(trifluoromethyl)benzyl alcohol (0.12 ml, 0.72 mmol), BuLi (1.00 ml, 1.55 mmol), N,N,N',N'-tetramethylethylenediamine (0.03 ml, 0.20 mmol) was added to 7 (352 mg, 0.53 mmol) in 2 ml of THF at -78 °C. After 10 min of stirring at that temperature, ca. 0.4 ml of the solution was transferred to an NMR tube by using a double ended needle (sample 1). Then the remaining solution was warmed to room temperature and was stirred for 24 h and ca. 0.4 ml of the mixture was transferred to an NMR tube (sample 2). ^{19}F NMR of both samples showed the same spectra at 0 °C, i.e., a pair of quartets (δ -76.0 and -76.4 ppm, (fig 1, upfield from $CFCl_3$)). The fact that only a pair of quartets was observed strongly suggested the formation of a hexacoordinate ate complex, in which each pair of CF_3 (a=a', b=b') should be magnetically identical, namely 1A or 1B. In order to discriminate the two possible structures, 12-crown-4 was added to the reaction mixture of 7 and 2 to deprive the ate complex of the lithium cation. ^{19}F NMR (470 MHz) of the solution showed a sharp singlet (δ -75.8 ppm), which indicated that the lithium ion was complexed with two cis oxygen atoms to keep the structure without 12-crown-4. Therefore, we assign the structure 1A for the complex, whereas the lithium ion cannot coordinate with the two trans oxygens in 1B. The complex 1A changed into symmetrical structure by removal of the lithium



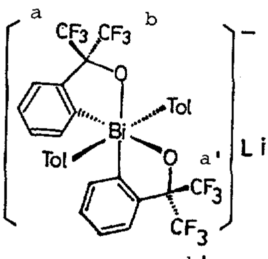
(eq 2)



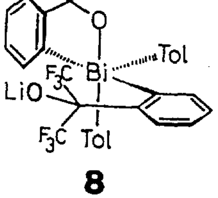
1B



1C



1D



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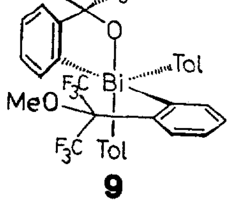

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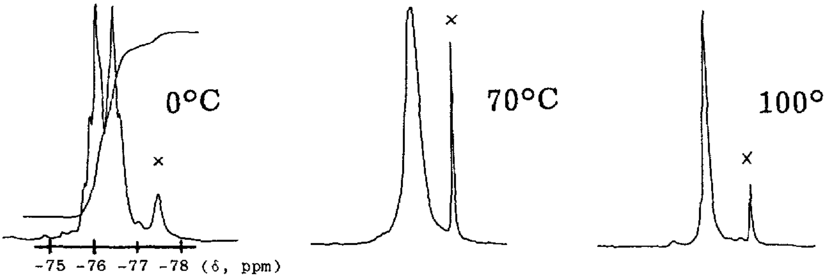
ion to show a sharp singlet of ^{19}F NMR, namely **1C** or **1D** (a=a'=b=b' magnetically).[9] The fact that ^{19}F NMR of **9** showed two sharp singlets at rather different field (δ -66.6 and -73.4 at 35 °C)[8] indicated that **1A** was <u>not</u> a pentacoordinated complex such as **8**.

The pair of quartets of the ate complex (**1A**) coalesced at 70 °C to become a singlet (fig. 1), which was stable up to 150 °C. The same quartets were observed again when the solution was cooled to 0 °C. This result clearly showed remarkable thermal stability of the ate complex in contrast to the reported instability of 12-Bi-6,[3,4] and in addition the ate complex observed in the reaction of **7** with **2** (samples 1 and 2) was concluded to be the most thermodynamically stable isomer, suggesting that equilibration to the isomer took place rather fast. This was supported by the fact that the same ^{19}F NMR spectrum was obtained for the complex prepared by the reaction of a bicyclic compound (**10**, vide infra) with p-$CH_3C_6H_4Li$. The activation energy of the equilibration was calculated from the ^{19}F NMR coalesce temperature to be 18 kcal/mol at 70 °C. The isomerization of the ate complexes may proceed through an intramolecular Bi-O bond cleavage by the lithium cation followed by pseudorotaion of the resulting 10-Bi-5 intermediate and recyclization similarly to that of 12-Sb-6 compound (scheme 1).[6]

The remarkable stability of the ate complex was also observed in the reaction of **1** with electrophiles. For example, 2.1 equiv of p-trifluoromethylbenzoyl chloride did not react with **1** even under refluxing in THF for 40 h. In the presence of 12-crown-4 p-chlorobenzoyl chloride did not react with **1** even after 13 h of stirring at room temperature and refluxing in THF for 4.5 h. At present only protons (such as water) reacted with **1** to give an alcohol **11**. It is interesting to note that **11** shows only one singlet (δ -74.5

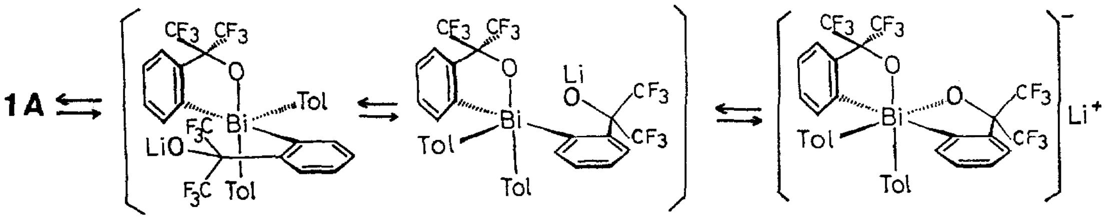
fig 1

^{19}F NMR of **1**



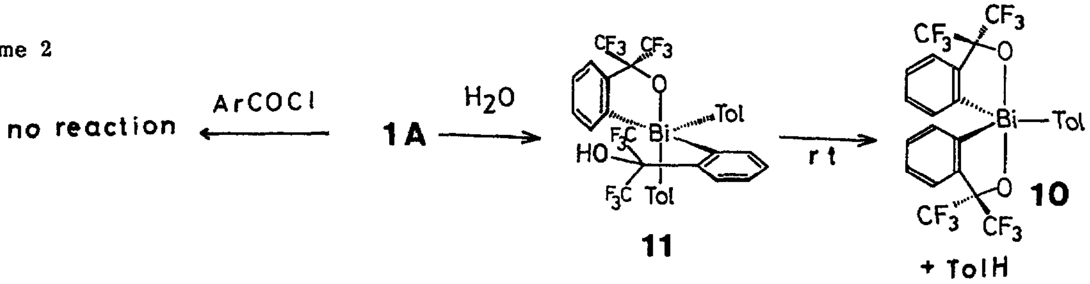
scheme 1

Mechanism for isomerization of **1**



($CDCl_3$)) in ^{19}F NMR at 0 °C, i.e., rapid bond switching takes place by intramolecular prototropy between the two oxygen atoms. The alcohol (11) is unstable at room temperature and cyclizes with elimination of toluene to afford a bicyclic compound 10 quantitatively.[10]

scheme 2



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8. 9 (prepared from 7 and 2-(2-lithiophenyl)-1,1,1,3,3,3-hexafluoro-2-methoxypropane): mp 232-234 °C. ^1H NMR ($CDCl_3$) δ 2.34 (s, 6 H), 3.28 (septet, 3 H, $^5J_{H-F}$=1Hz), 7.0-8.1 (m, 16 H). Anal. Calcd for $C_{33}H_{25}BiF_{12}O_2$: C, 44.51; H, 2.83. Found: C, 44.40; H, 2.78. ^{19}F NMR ($CDCl_3$) δ -66.6 (s, 6 F), -73.4 (s, 6 F). A fact that each signal splits into a pair of quartets at -67 and -40 °C, respectively, indicated weak coordination between the oxygen atom of the methoxy group and the central bismuth atom.
9. We do not have any evidence for the structure of 1 in the presence of 12-crown-4. Two structures 1C and 1D are possible, in which all four CF_3 groups are magnetically identical.
10. 11: ^1H NMR ($CDCl_3$) δ 2.35 (s, 6 H), 7.1-8.1 (m, 16 H). ^{19}F NMR ($CDCl_3$) δ -74.5 (s). 10: mp 130-132 °C. ^1H NMR ($CDCl_3$) δ 2.37 (s, 3 H), 7.30-8.15 (m, 12 H). ^{19}F NMR ($CDCl_3$) δ -75.2 (q, 6 F, J=8Hz), -74.0 (q, 6 F, J=8Hz). Anal. Calcd for $C_{25}H_{15}BiF_{12}O_2$: C, 38.28; H, 1.93. Found: C, 38.21; H, 1.95.
11. Partial support of this research is acknowledged for Grant-in-Aids for Special Project Research (No. 61225019 and No. 62215026) by the Ministry of Education, Science and Culture of the Japanese Government. We are grateful to Central Glass Co. Ltd. for gift of hexafluorocumyl alcohol.

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