Structure of Azabismocines, Hexacoordinate Pentavalent Organobismuth Compounds

Mao Minoura, Yuka Kanamori, Akira Miyake, and Kin-ya Akiba*
Department of Chemistry, Graduate School of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739-8526

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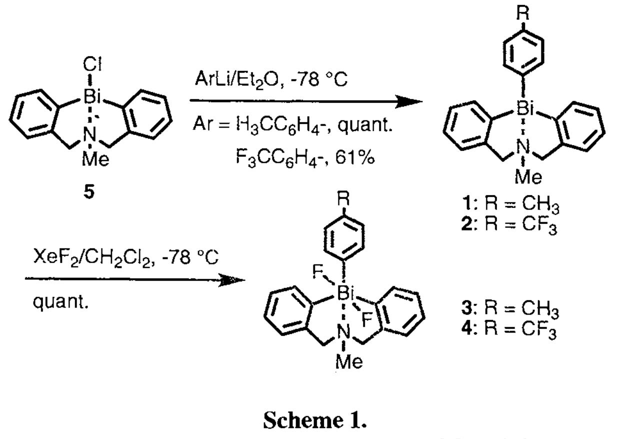
Azabisomocine derivatives having a pentavalent bismuth and a nitrogen at 1,5-position were synthesized. The X-ray structural analysis reveals that these compounds have hexacoordinate distorted octahedral geometry which is caused by transannular bond formation between the bismuth and the nitrogen.

There has been much interest in organobismuth compounds because of their synthetic utility and unique structural features which are correlated with hypervalency of the bismuth.[1] In connection with our program investigating the chemistry of hypervalent compounds,[2] we had occasion to prepare dibenz[*c,f*][1,5]-azastibocine and -azabismocine derivatives.[3] The transannular interaction at 1,5-position of the eight membered ring has been studied by means of NMR spectroscopy and the formation of a hypervalent bond in those heterocycles has been revealed. In spite of those studies on hypervalent Bi^{V}, structurally characterized hexacoordinate Bi^{V} compounds are relatively scarce.[4] We present here low temperature X-ray structural characterization of dibenz[*c,f*][1,5]-azabismocine compounds bearing hexacoordinate Bi^{V}.

Difluoroazabismocine derivatives **3** and **4** were obtained by the oxidative-addition reaction of xenon difluoride with trivalent azabismocine **1** and **2** which were prepared from chloroazabismocine **5** with corresponding aryllithium, respectively (Scheme 1).[5] The difluorides can also be prepared by the halogen exchange using KF with corresponding dichlorides which are obtained from the reaction of SOCl with **1** or **2**. The former method gave better results than the latter.



Scheme 1.

In solution, the methylene protons of **3** and **4** appear as an AB quartet (J = 14.2 Hz). In ^{19}F NMR spectra of **3** and **4**, an AB quartet (J = 120 Hz) with large difference of the chemical shifts is observed in two fluorines on the bismuth atom, indicating that those fluorines are inequivalent due to the fixation of the NMe group by the transannular interaction between Bi and N.

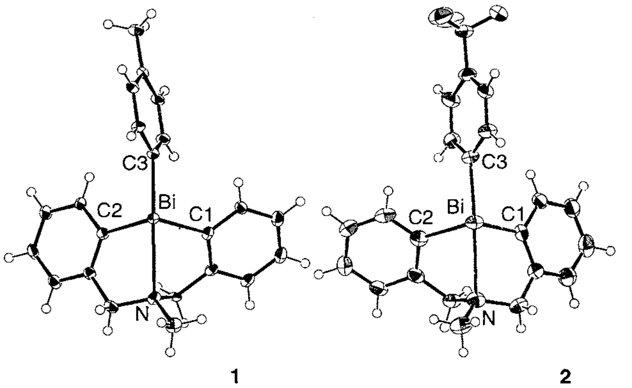


Figure 1. ORTEP drawings of trivalent azabismocine **1** and **2** with 50% probability level.

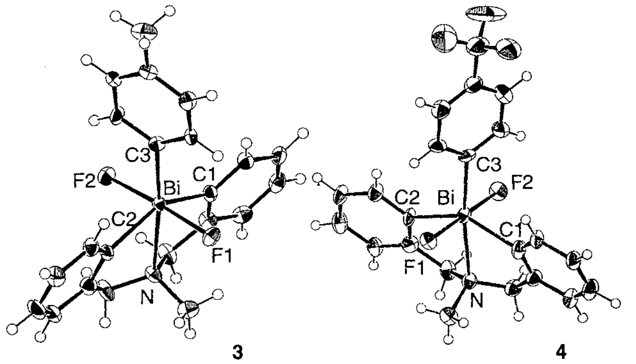


Figure 2. ORTEP drawings of pentavalent azabismocines **3** and **4** with 50% probability level. Acetonitrile molecule in **4** is omitted for clarity.

The X-ray structural analysis of pentavalent azabismocines **3** and **4** was performed at 130 K and also that of trivalent analogues **1** and **2** for comparison. Figures 1 and 2 show molecular structure of **1** – **4**.[6] Selected bond lengths and angles of **1** – **4** are listed in Table 1.

Transannular bond formation is found between Bi and N atoms in both tri- and pentavalent azabismocines **1** – **4**. Their Bi-N distances, 2.78–2.58 Å, are much shorter than the sum of their van der Waals radii 3.9 Å and larger than that of their covalent bond radii 2.22 Å.[7] The Bi-N distaneces become shorter acccording to the increase of oxidation state of the Bi atom and electron-withdrawing character of the substituent at *trans* position of the nitrogen, that is, Bi-N distance of **4** having pentavalent Bi with CF_3 group, 2.63 Å, is the shortest among them. These results indicate the hypervalent bond formation between Bi and N which is influenced by the electronic property of aryl groups on the Bi atom. By the increase of oxidation state of the bismuth from III to V, the bond distance of Bi-C also shortens by 0.06 Å (av.), on the other hand, bond angle of C1-Bi-C2 enlarges from 102° to 144° and that of N-Bi-C3 does so from 152° to 173°. The bond angle of F1-Bi-F2 is 176°. These facts show that quite distorted pseudo trigonal bipyramidal (TBP) structure of **1** and **2** bearing lone pair electrons was changed to the distorted octahedral (Oh) structure of **3** and **4** according oxidation of the bismuth atom along with N-Bi bond formation. The large distortion of the structure from ideal Oh (**3** and **4**) may certainly be due to the fundamental strain caused by dibenzazabismocine skeleton.

Table 1. Selected bond lengths (Å) and angles (°)

	1	**2**[a]	**3**[a]	**4**
Bi-N	2.780(2)	2.764(5) [2.733(5)]	2.613(4) [2.618(4)]	2.579(4)
Bi-C1	2.254(2)	2.240(4) [2.244(4)]	2.196(5) [2.186(4)]	2.174(4)
Bi-C2	2.272(2)	2.265(4) [2.296(5)]	2.175(5) [2.200(5)]	2.199(4)
Bi-C3	2.272(2)	2.266(5) [2.268(5)]	2.210(4) [2.224(4)]	2.225(5)
Bi-F1	—	—	2.114(3) [2.128(3)]	2.132(3)
Bi-F2	—	—	2.163(4) [2.147(4)]	2.134(3)
C1-Bi-C2	101.7(1)	102.3(2) [102.2(2)]	143.8(2) [144.1(2)]	144.9(2)
N-Bi-C3	150.0(1)	153.4(2) [152.4(2)]	174.6(2) [173.2(2)]	171.8(2)
F1-Bi-F2	—	—	174.3(2) [176.4(2)]	178.1(2)

[a] One of the two independent molecules in the unit cell is shown in square brackets.

The thermal ligand coupling reaction has been shown as one of the typical reaction of pentavalent group 15 compound.[8] The thermolysis of pentavalent **3** and **4** proceeded at 130 °C in acetonitrile solution to give ligand coupling products, i. e., corresponding fluoroarene (ca. 70%) and monofluoro-azabismocine (quantitatively). Interestingly, when tris(4-methylphenyl)bismuth difluoride was subjected to thermolysis under the same conditions, the ligand coupling reaction did not occur. These results suggest that the N-Bi bond in **3** and **4** assisted the ligand coupling reaction.

Detailed results will be described elsewhere including related materials.

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References and Notes

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5 All new compounds gave satisfactory C, H, N elemental analyses. Compound **1**: colorless crystals, mp 152-155 °C, ^{1}H NMR(CDCl$_3$, 400 MHz) δ 2.39(s, 3H), 2.50(s, 3H), 3.70, 3.90(ABq, J = 14.3 Hz, 4H), 7.10-7.28(m, 8H), 7.59(d, J = 7.8 Hz, 2H), 7.76(d, J = 7.8 Hz, 2H), ^{13}C NMR(CDCl$_3$, 100 MHz) δ 21.8, 42.1, 62.2, 127.1, 128.0, 129.3, 130.8, 136.7, 139.0, 139.4, 146.2, 153.4, 162.5. Compound **2**: pale yellow crystals, mp 163-164 °C, ^{1}H NMR(CDCl$_3$, 400 MHz) δ 2.53(s, 3H), 3.78, 3.90(ABq, J = 14.5 Hz, 4H), 7.0-7.6(m, 8H), 7.68(d, J = 7.2 Hz, 2H), 8.00(d, J = 7.2 Hz, 2H), ^{19}F NMR(CDCl$_3$, 376 MHz) δ –62.9(s, 3F), ^{13}C NMR(CDCl$_3$, 100 MHz) δ 42.1, 62.2, 124.8(q, $^1J_{CF}$ = 270.2 Hz), 126.1, 127.4, 128.2, 129.2(q, $^2J_{CF}$ = 31.2 Hz), 129.6, 138.9, 139.7, 146.3, 153.9, 171.2. Compound **3**: colorless crystals, mp 189-190 °C, ^{1}H NMR(CDCl$_3$, 400 MHz) δ 2.37(s, 3H), 2.47(s, 3H), 4.11, 4.51(ABq, J = 14.0 Hz, 4H), 7.2-7.5(m, 8H), 7.68(d, J = 7.8 Hz, 2H), 8.04(d, J = 7.8 Hz, 2H), ^{19}F NMR(CDCl$_3$, 376 MHz) δ –134.0, –142.8(ABq, J = 120 Hz, 2F), ^{13}C NMR(CDCl$_3$, 100 MHz) δ 21.4, 39.6, 59.7, 130.5, 131.1, 131.6, 132.3, 135.2, 137.6, 141.3, 148.8, 159.1. Compound **4**: pale yellow crystals, mp 187-188 °C, ^{1}H NMR(CDCl$_3$, 400 MHz) δ 2.40(s, 3H), 4.19, 4.53(ABq, J = 14.2 Hz, 4H), 7.2-7.7(m, 8H), 7.96(d, J = 7.8 Hz, 2H), 8.36(d, J = 7.8 Hz, 2H), ^{19}F NMR(CDCl$_3$, 376 MHz) δ –63.4(s, 3F), –132.4, –141.7(ABq, J = 120 Hz, 2F), ^{13}C NMR(CDCl$_3$, 100 MHz) δ 39.5, 59.4, 123.8(q, $^1J_{CF}$ = 272.9 Hz), 127.13, 127.16, 130.7, 131.5, 132.2, 133.0(q, $^2J_{CF}$ = 33.1 Hz), 135.9, 137.5, 157.5, 158.1.

6 Crystal data for **1**: $C_{22}H_{22}NBi$, M = 509.40, *monoclinic*, space group $P2_1/a$, a = 10.8880(4), b = 14.7640(4), c = 11.5790(4) Å, β = 100.084(2)°, V = 1832.5(1) Å^3, Z = 4, D_{calc} = 1.846 g/cm^3, R = 0.041 (Rw = 0.046) for 4026 observed reflections (218 parameters). Crystal data for **2**: $C_{22}H_{19}NF_3Bi$, M = 563.37, *triclinic*, space group $P\bar{1}$, a = 10.939(1), b = 13.4370(9), c = 14.355(1) Å, α = 66.378(5), β = 87.398(5), γ = 86.519(5)°, V = 1929.1(3) Å^3, Z = 4, D_{calc} = 1.940 g/cm^3, R = 0.052 (Rw = 0.059) for 6633 observed reflections (488 parameters). Crystal data for **3**: $C_{22}H_{22}NF_2Bi$, M = 547.40, *orthorhombic*, space group *Pbca*, a = 9.6870(1), b = 16.1830(5), c = 49.896(2) Å, V = 7821.9(3) Å^3, Z = 16, D_{calc} = 1.859 g/cm^3, R = 0.031 (Rw = 0.039) for 6427 observed reflections (470 parameters). Crystal data for **4**·MeCN: $C_{24}H_{22}N_2F_5Bi$, M = 642.42, *orthorhombic*, space group *Pcab*, a = 12.0350(3), b = 16.2400(6), c = 23.514(1) Å, V = 4595.7(2) Å^3, Z = 8, D_{calc} = 1.857 g/cm^3, R = 0.041, (Rw = 0.046) for 4206 observed reflections (290 parameters). All data were collected at 130 K on a MAC Science DIP2030 imaging plate with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved using the Crystan-GM system and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included at calculated positions but not refined.

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