Cationic Organobismuth Complex with 5,6,7,12-Tetrahydrodibenz[*c,f*][1,5]azabismocine Framework and Its Coordination Complexes with Neutral Molecules

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Received December 19, 2006

A cationic eight-electron three-coordinate organobismuth complex with a weakly coordinating borate anion, $[^tBuN(CH_2C_6H_4)_2Bi]^+[B(C_6F_5)_4]^-$ (**3**), and its coordination complexes with neutral donor molecules were synthesized and structurally characterized. The reaction of $^tBuN(CH_2C_6H_4)_2Bi{-}X$ (**1a**: X = Br, **1b**: X = Cl) with $Li[B(C_6F_5)_4]$ afforded the ionic complex **3**. Complex **3** reacted with **1a** or **1b** to form halogen-bridged dinuclear complexes $[\{^tBuN(CH_2C_6H_4)_2Bi\}_2(\mu\text{-}X)]^+[B(C_6F_5)_4]^-$ (**6**: X = Br, **7**: X = Cl). Various neutral donor molecules coordinated to the cationic bismuth atom of **3**, and four coordination complexes $[\{^tBuN(CH_2C_6H_4)_2Bi\}(Do)]^+[B(C_6F_5)_4]^-$ (**8**: Do = MeCHO, **9**: Do = MeOH, **10**: Do = MeCN, **11**: Do = CH_2Cl_2) were isolated. The structures of complexes **3** and **6**−**11** were determined by single-crystal X-ray analysis. In complex **3**, one of the fluorine atoms of the $[B(C_6F_5)_4]$ anion weakly coordinates to the cationic bismuth center, making its coordination geometry equatorially vacant trigonal bipyramidal. The same coordination geometry was also found for the bismuth centers in **6**−**11**. The cationic character of the bismuth center in **3** is reflected in the Bi−N coordination distance, which is ≥0.2 Å shorter than those in the neutral azabismocines such as **1a** and **1b**. The Bi−N coordination distances in **6**−**11** elongated depending on the coordination strength of the donor molecules.

Introduction

Cationic organometallic complexes of transition and main group metals have been widely used as catalysts for polymerization and organic synthesis.[1−6] Since inorganic bismuth compounds such as bismuth triflate and halides have attracted recent interest as efficient Lewis acid catalysts for organic synthesis,[7−9] cationic organobismuth compounds will provide potentially useful catalysts. However, the study on cationic organobismuth complexes is very limited,[10−18] and their application to catalysis has not been reported. This is partly because of the instability of organobismuth compounds that have weak Bi−C bonds.[19] We have been interested in using organobismuth compounds as reagents and catalysts for organic transformations. We have searched organobismuth compounds having stable cyclic frameworks for this purpose and recently reported that hypervalent organobismuth compounds, 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azabismocines,[20−22] are useful and recoverable reagents for the cross-coupling reaction with organic bromides and chlorides.[23,24] Since the 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azabismocine framework is very stable, we thought cationic 5,6,7,12-tetrahydrodibenz[*c,f*][1,5]azabismocines were useful compounds to examine the structure and reactivity of cationic organobismuth compounds as potential catalysts. Here we report the synthesis and structure of a cationic 5,6,7,12-

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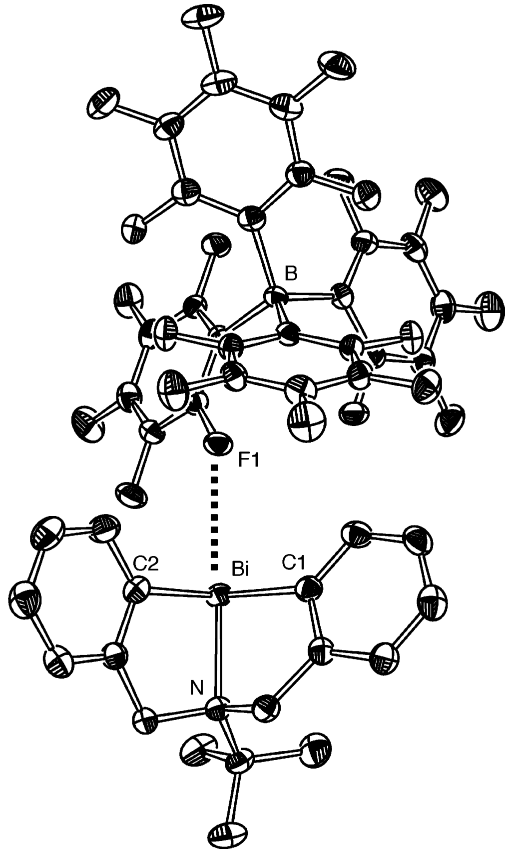
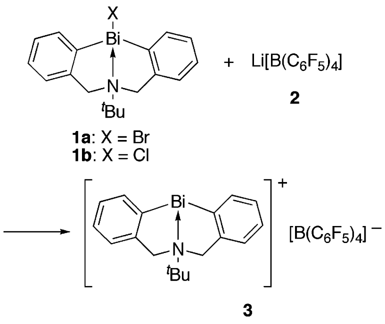


Figure 1. Structure of complex **3** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity.

Scheme 1

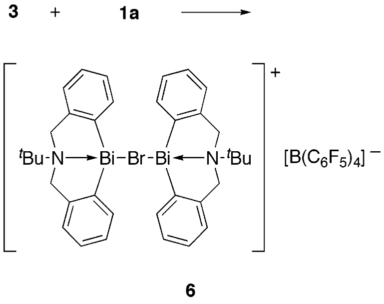


tetrahydrodibenz[*c*,*f*][1,5]azabismocine with a weakly coordinating borate anion and its coordination behavior with some neutral donor molecules, giving isolable coordination complexes.

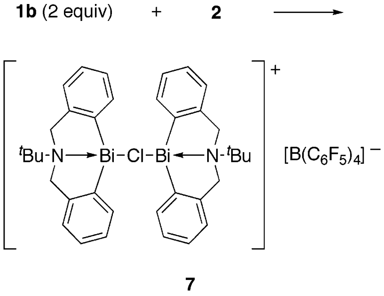
Results and Discussion

A cationic eight-electron three-coordinate bismuth complex with a weakly coordinating borate anion, $[{}^t\mathrm{BuN(CH_2C_6H_4)_2Bi}]^+[\mathrm{B(C_6F_5)_4}]^-$ (**3**), was almost quantitatively obtained by the reaction of bismuth bromide **1a** or chloride **1b** with $\mathrm{Li[B(C_6F_5)_4]}$ (**2**) in CH_2Cl_2 (Scheme 1). Recrystallization from CH_2Cl_2/hexane gave crystals suitable for single-crystal X-ray analysis. Figure 1 shows an ellipsoid plot of complex **3**. Selected bond distances and angles are summarized in Table 1. In the solid state, one of the fluorine atoms of the anion occupies a vacant site of the cationic bismuth center, making its coordination geometry distorted equatorially vacant trigonal bipyramidal with the nitrogen and the fluorine atoms in the apical positions and the two carbon atoms in the equatorial positions. The Bi$\cdots$F distance in **3** (2.971(2) Å) is ca. 20% shorter than the sum of van der Waals radii (3.75 Å)[25] and much longer than covalent Bi−F bond distances (2.190(4) Å in $^t\mathrm{BuN(CH_2C_6H_4)_2Bi{-}F}$,[22] 2.088(8)−2.59(1) Å in the literature[18,21,26−32]). Weak interactions between the metals and fluorine atoms of fluorocarbons are well known.[33] For bismuth compounds, Bi$\cdots$F (fluorocarbons) short contacts were reported in some neutral and an anionic bismuth compound.[33−36]

Scheme 2



Scheme 3



Scheme 4

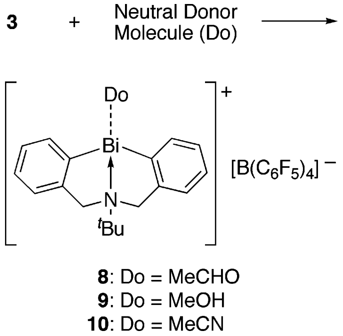


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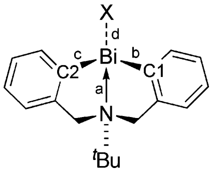
Table 1. Selected Bond Distances (Å) and Angles (deg) for 1a, 1b, 3, and 6−11



bond/ angle	**1a**[a]	**1b**[a]	**3**	**6**		**7**		**8**[b]		**9**	**10**	**11**
a	2.559(4)	2.568(3)	2.357(2)	2.457(6)	2.475(6)	2.470(4)	2.487(4)	2.388(6)	2.402(6)	2.419(6)	2.400(3)	2.384(4)
b	2.247(5)	2.241(3)	2.221(3)	2.238(7)	2.230(7)	2.238(5)	2.225(6)	2.238(7)	2.205(7)	2.233(8)	2.235(4)	2.227(5)
c	2.247(5)	2.250(5)	2.223(3)	2.230(7)	2.233(7)	2.227(5)	2.246(5)	2.227(8)	2.211(8)	2.211(8)	2.223(3)	2.210(5)
d	2.7912(5)	2.663(1)	2.971(2) (Bi···F)	2.9921(8) (Bi···Br)	2.8800(9) (Bi···Br)	2.879(1) (Bi···Cl)	2.766(1) (Bi···Cl)	2.612(7) (Bi···O)	2.589(7) (Bi···O)	2.584(9) (Bi···O)	2.661(3) Bi···N)	3.250(3) (Bi···Cl)
ab	75.3(1)	75.1(1)	79.4(1)	74.8(2)	75.7(2)	74.2(2)	75.6(2)	76.3(2)	78.3(2)	75.3(2)	75.9(1)	75.7(2)
ac	72.9(1)	73.1(1)	76.9(1)	76.5(2)	74.3(2)	76.6(2)	74.3(2)	77.4(3)	75.4(3)	77.2(2)	77.7(1)	78.7(2)
ad	159.83(9)	158.73(9)	156.67(7)	153.0(1)	157.4(1)	153.2(1)	156.1(1)	160.6(2)	149.9(2)	152.8(3)	151.6(1)	148.5(1)
bc	93.9(2)	93.6(1)	96.2(1)	99.2(3)	100.5(3)	98.4(2)	100.5(2)	97.4(3)	97.7(3)	97.5(3)	99.4(1)	98.3(2)
bd	91.4(1)	90.8(1)	86.48(9)	88.8(2)	90.1(2)	88.9(1)	89.5(1)	89.2(2)	79.7(3)	87.3(3)	86.4(1)	88.5(1)
cd	93.4(1)	92.4(1)	86.41(9)	85.4(2)	91.5(2)	85.8(1)	90.6(1)	91.9(3)	87.5(3)	84.8(3)	83.6(1)	76.8(1)

[a] Ref 22. [b]Two independent molecules in the unit cell.

It is known that the intramolecular Bi−N coordination distances of 5,6,7,12-tetrahydrodibenz[*c*,*f*][1,5]azabismocines are highly affected by the electronic nature of the Bi atom.[21,22] We showed the Bi−N distances in 5,6,7,12-tetrahydrodibenz[*c*,*f*]-[1,5]azabismocines have a good linear relationship against Hammett's σ_m-constants of the substituents on the Bi atom.[22] As expected, X-ray diffraction showed the Bi−N distance (2.357(2) Å) in the cationic complex **3** is much shorter than those of previously reported neutral 5,6,7,12-tetrahydrodibenz-[*c*,*f*][1,5]azabismocines (2.559(4)−2.894(4) Å).[21,22] The Bi−N distance in **3** is also much shorter than those (2.491(1) and 2.509(1) Å) of the cationic organobismuth complex [{2-(Me_2NCH_2)C_6H_4}$_2$Bi][PF_6] (**4**), in which the cationic bismuth center is coordinated by the two amino groups.[14] The precursors of **3** and **4**, i.e., neutral bismuth chlorides **1b** and **5**[37] (in the latter compound only one amino group coordinates to the bismuth center), have similar bismuth coordination geometries and their Bi−N distances (2.568(3) and 2.570(5) Å, respectively) are almost identical. Therefore, the significant difference in the Bi−N distances of **3** and **4** is not caused by the incorporation of the amino group in the eight-membered azabismocine ring in **3**, but is simply coming from the presence of the second coordinating amino group in **4**.

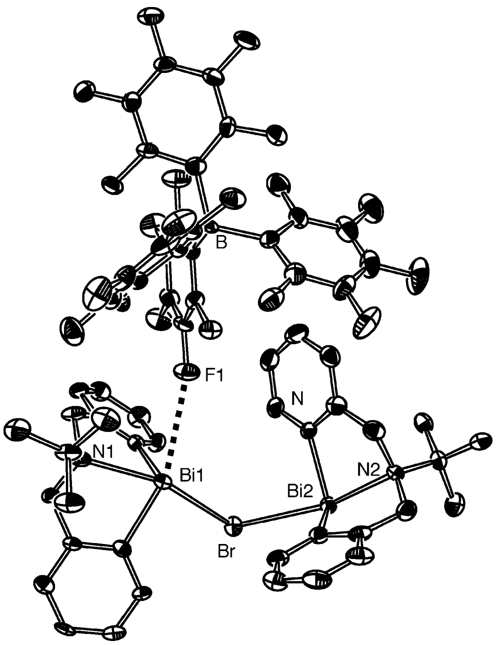
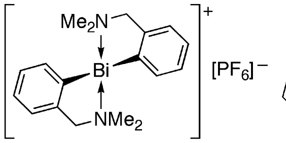


Figure 2. Structure of complex **6** (50% probability ellipsoids). Hydrogen atoms and CH_2Cl_2 are omitted for clarity.



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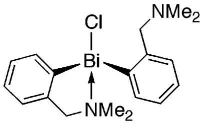

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During the X-ray analysis of **3**, we observed the presence of a tiny amount of byproduct, bromine-bridged dinuclear cationic complex **6**, which was probably formed by the reaction of **3** with **1a** used in slight excess. Indeed, the reaction of **3** with **1a** in 1:1 ratio in CH_2Cl_2 afforded **6** in 83% isolated yield (Scheme 2). A similar chlorine-bridged dinuclear complex, **7**, was also synthesized in 85% isolated yield by the reaction of **1b** and **2** in 2:1 ratio (Scheme 3). Complexes **6** and **7** afforded isomorphous crystals containing solvent molecules by recrystallization from CH_2Cl_2. Selected bond distances and angles of **6** and **7** are shown in Table 1. Figure 2 shows the structure of **6**, in which two azabismocine units are asymmetrically bound to the bromine atom. The Bi1−Br distance is 0.11 Å longer than the Bi2−Br distance, while the Bi1−N distance is ca. 0.02 Å shorter than the Bi2−N distance. The Bi1−Br and Bi2−Br distances are respectively 0.20 and 0.09 Å longer than the Bi−Br distance in **1a**, while Bi1−N and Bi2−N distances are respectively 0.10 and 0.08 Å shorter than the Bi−N distance in **1a**. These results probably suggest that Bi1 has higher cationic character than Bi2 and may be reflected in the fact that one of the fluorine atoms of the anion is located relatively near Bi1 (Bi1···F1 = 3.217(4) Å, within the sum of van der Waals radii of Bi and F atoms (3.75 Å)). Very similar structural trends were observed for the chlorine-bridged complex **7**.

In order to obtain further information on the coordination ability of **3** as well as the coordination effect of donor molecules on the structure of **3**, we have examined the reaction of **3** with

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Table 2. Crystallographic Data for Complexes 3 and 6−11

	3	**6**	**7**	**8**	**9**	**10**	**11**
formula	$C_{42}H_{21}BBiF_{20}N$	$C_{61}H_{44}BBi_2BrCl_2F_{20}N_2$	$C_{61}H_{44}BBi_2Cl_3F_{20}N_2$	$C_{44}H_{25}BBiF_{20}NO$	$C_{43}H_{25}BBiF_{20}NO$	$C_{44}H_{24}BBiF_{20}N_2$	$C_{43}H_{23}BBiCl_2F_{20}N$
fw	1139.39	1764.58	1720.13	1183.45	1171.43	1180.45	1224.33
cryst size	0.45 × 0.28 × 0.07	0.32 × 0.06 × 0.02	0.16 × 0.11 × 0.02	0.32 × 0.06 × 0.02	0.28 × 0.05 × 0.01	0.14 × 0.09 × 0.06	0.16 × 0.13 × 0.10
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$Pca2_1$	$Pbca$ (#61)	$P2_1/c$ (#14)	$Pbca$ (#61)
a/Å	14.655(1)	10.0830(6)	10.0838(5)	21.409(2)	21.248(1)	16.1503(9)	21.3142(10)
b/Å	18.220(3)	14.7480(9)	14.8011(8)	24.581(3)	15.8200(11)	19.3680(10)	15.8821(8)
c/Å	14.726(2)	39.812(2)	39.526(2)	15.709(2)	24.374(2)	13.6021(7)	24.2633(12)
β/deg	98.600(8)	92.0560(10)	91.8310(10)	90	90	105.5520(10)	90
V/Å	3887.8(9)	5916.4(6)	5896.4(5)	8266.9(15)	8193.3(10)	4098.9(4)	8213.5(7)
Z	4	4	4	8	8	4	8
D_{calc}/g cm^{-3}	1.946	1.981	1.938	1.902	1.899	1.913	1.980
F(000)	2192.00	3376.00	3304.00	4576.00	4528.00	2280.00	4720.00
μ(Mo Kα)/cm^{-1}	46.58	68.03	61.92	43.87	44.25	44.22	45.43
T/K	173(2)	153(2)	153(2)	153(2)	153(2)	153(2)	153(2)
$2\theta_{max}$/deg	55.0	56.4	56.5	56.6	56.5	56.6	56.6
no. of rflns measd	9542	36 435	35 696	49 792	50 694	25 521	51 220
no. of unique rflns (R_{int})	8903 (0.024)	13 799 (0.065)	13 665 (0.042)	17 414 (0.050)	9738 (0.086)	9609 (0.033)	9758 (0.045)
no. of variables	608	846	846	1227	605	614	614
R1 ($I_o > 2.0\sigma(I_o)$)	0.024	0.046	0.042	0.044	0.063	0.034	0.045
wR2 (all data)	0.065	0.098	0.080	0.106	0.139	0.080	0.135
GOF	1.025	1.057	1.000	1.046	1.072	1.028	1.070
diff peak, hole/e Å^{-3}	1.08, −1.02	2.24, −1.95	2.17, −2.66	6.93, −3.44	2.00, −1.80	1.13, −0.61	2.31, −1.99

some neutral donor molecules. Aldehydes, MeOH, and MeCN formed isolable coordination complexes with **3** (Scheme 4). Among three aldehyde complexes (benzaldehyde, acetaldehyde, and propionaldehyde), X-ray-quality single crystals were obtained for acetaldehyde complex **8** by the crystallization of **3** in the presence of acetaldehyde (4 equiv) from a CH_2Cl_2/hexane mixture at −25 °C. MeOH and MeCN relatively strongly coordinate to cation **3** and afforded coordination complexes **9** and **10**, respectively, by removal of solvent from a CH_2Cl_2 solution of **3** and ca. 1.2 equiv of MeOH or MeCN.

Figure 3 shows the structure of the acetaldehyde-coordinated cationic part of complex **8**. Although a number of aldehyde-coordinated cationic complexes of transition and main group metals have been structurally characterized by X-ray analysis, no aldehyde-coordinated bismuth complex is found in the CSD.[38] Structures of some ketone-coordinated neutral and anionic bismuth complexes were reported.[39−41] The Bi···O distance in **8** (2.60 Å, average) is more than 30% shorter than the sum of van der Waals radii (3.80 Å);[25] it is shorter than those (2.69−2.72 Å) in acetone complexes of $[Bi_2X_8]^{2-}$ anions (X = Cl, Br)[40,41] and longer than the intramolecular Bi···O distance (2.52 Å) in a neutral compound, (2-$MeCOC_6H_4$)(4-MeC_6H_4)BiBr.[39] The coordination of acetaldehyde slightly (0.038 Å in average) lengthened the intramolecular Bi−N coordination distance compared with that of **3**.

Figure 4 shows the structure of the MeOH-coordinated cationic part of complex **9**. The Bi···O distance in **9** is slightly shorter than those in acetaldehyde complex **8**, and in turn the Bi−N distance in **9** is slightly longer than those in **8**. There are three examples of MeOH-coordinated Bi complexes in the CSD,[38] and the Bi···O distance in **9** is within their range (2.55−2.71 Å).[42−44]

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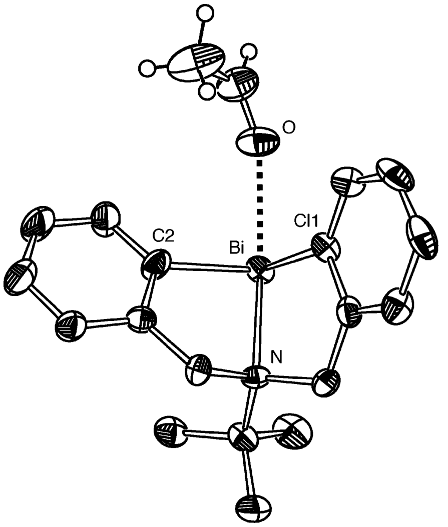

Figure 3. Structure of the cationic part of complex **8** (50% thermal ellipsoids for Bi, C, N, and O atoms). Hydrogen atoms except those of acetaldehyde are omitted for clarity.

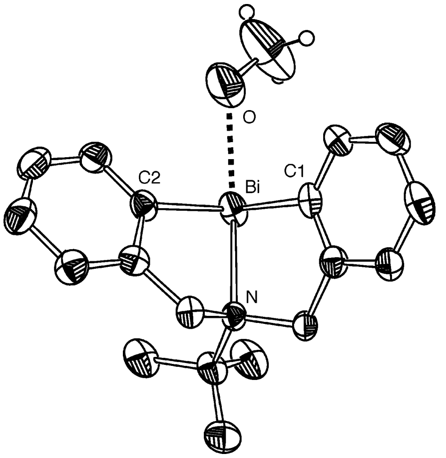

Figure 4. Structure of the cationic part of complex **9** (50% thermal ellipsoids for Bi, C, N, and O atoms). The hydrogen atom of the OH group could not be located. Hydrogen atoms except those of methanol are omitted for clarity.

Figure 5 shows the structure of the MeCN-coordinated cationic part of complex **10**. There are three examples of MeCN-coordinated Bi complexes in the CSD,[38] and the Bi···NCMe coordination distance in **10** is almost identical to those found in $[BiCl_2([15]crown\text{-}5)(MeCN)][SbCl_6]$ (2.65(3) Å)[45] and $[Bi([12]crwon\text{-}4)_2(MeCN)][SbCl_6]_3$ (2.650(9) Å).[46] Elongation of the Bi−N distance is almost the same as that in acetaldehyde complex **8**.

The crystallization of **3** in the presence of Ph_2O or Ph_2S in CH_2Cl_2 did not afford a Ph_2O- or Ph_2S-coordinated complex but instead gave CH_2Cl_2-coordinated complex **11**. It is worth noting that CH_2Cl_2-free complex **3** was obtained by recrystallization of **3** from a CH_2Cl_2/hexane mixture as mentioned above, while that of **3** from CH_2Cl_2 solution in the presence of Ph_2O or Ph_2S afforded CH_2Cl_2-coordinated complex **11**. The reason is not clear why this difference occurred. Although the coordination of CH_2Cl_2 as a monodentate or a bidentate ligand to metals is known, isolated examples of such metal complexes are limited to transition metals (22 examples in the CSD)[38,47−51] and alkali metals (2 examples in the CSD),[52,53] and no example is found for group 12−16 elements in the CSD. Figure 6 shows the structure of the CH_2Cl_2-coordinated cationic part of complex **11**, in which the vacant coordination site of the bismuth center is occupied by one of the chlorine atoms of CH_2Cl_2. The Bi···Cl distance (3.250(3) Å) is about 23% shorter than the sum of van der Waals radii (4.21 Å).[25] The other chlorine atom is also located near the bismuth center (3.446(2) Å), which may suggest

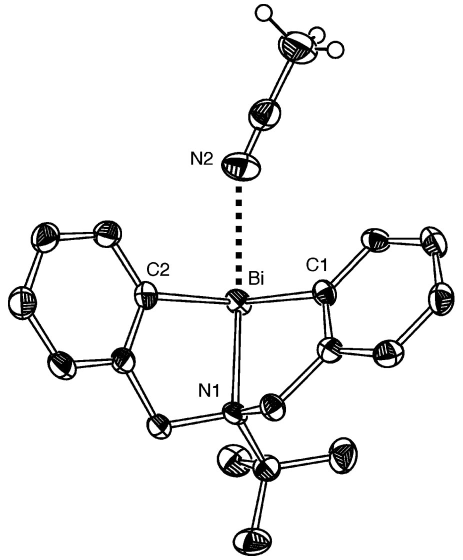

Figure 5. Structure of the cationic part of complex **10** (50% thermal ellipsoids for Bi, C, N, and O atoms). Hydrogen atoms except those of MeCN are omitted for clarity.

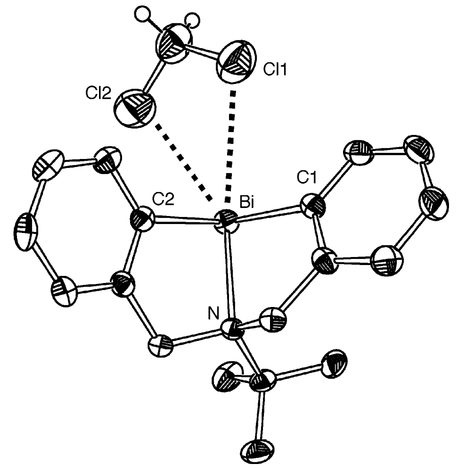

Figure 6. Structure of the cationic part of complex **11** (50% thermal ellipsoids for Bi, C, Cl, and N atoms). Hydrogen atoms except those of CH_2Cl_2 are omitted for clarity.

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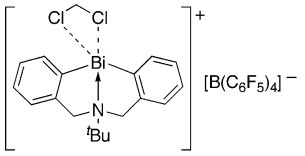
bidentate coordination of the CH_2Cl_2 ligand as observed in several examples.[48,49,52,54,55]



11

Conclusion

We have succeeded in synthesizing a stable cationic eight-electron three-coordinate organobismuth complex with a weakly coordinating anion, $[{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, **3**. In the solid state, one of the fluorine atoms of the anion in **3** weakly coordinates to the bismuth to form a 10-electron four-coordinate center. Complex **3** accepts various neutral molecules, such as aldehydes, methanol, acetonitrile, and dichloromethane, to form isolable coordination complexes. The coordination of the donor molecules elongates the intramolecular nitrogen to bismuth coordination distance, and the degree of elongation depends on their coordination strength. This adjustable property of the intramolecular nitrogen to bismuth coordination stabilizes the cationic complex and is potentially useful for catalysis.[56]

Experimental Details

General Comments. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques or in a glovebox filled with argon or nitrogen. Anhydrous solvents were purchased from Kanto Chemicals or Aldrich and used as received. $\mathrm{Li}[\mathrm{B}(\mathrm{C_6F_5})_4]$ was purchased from Tosoh Finechem. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol LA500 spectrometer. Chemical shifts given in ppm are referenced to tetramethylsilane (external) for ^{1}H and ^{13}C NMR spectra (0.0 ppm), and coupling constants are reported in hertz.

$[{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 3. To a slurry of $\mathrm{Li}[\mathrm{B}(\mathrm{C_6F_5})_4]$ (1.0 mmol, 686 mg) in 10 mL of CH_2Cl_2 at −20 °C was added a cooled (−20 °C) solution of bismuth chloride **1b** (1.0 mmol, 496 mg) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at −20 °C for 2 h and then allowed to warm slowly to room temperature. The precipitated LiCl was removed by filtration, and the solvent was removed under vacuum to give compound **3** quantitatively. Further purification by recrystallization from CH_2Cl_2/hexane furnished **3** as colorless crystals (1.06 g, 93%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 8.12 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.73 (t, J = 7.5 Hz, 2H), 7.53 (td, J = 7.5, 1.2 Hz, 2H), 5.00 (d, J = 15.5 Hz, 2H), 4.72 (d, J = 15.5 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 184.0, 155.3, 148.6 (d, J_{CF} = 241 Hz), 138.7 (d, J_{CF} = 242 Hz), 138.0, 136.7 (d, J_{CF} = 243 Hz), 132.8, 130.3, 129.5, 124.6 (bs), 66.5, 65.7, 28.6. IR (KBr): 2978, 1644, 1514, 1464, 1275, 1086, 980, 756 cm^{-1}. Anal. Calcd for $C_{42}H_{21}BBiF_{20}N$: C, 44.27; H, 1.86; N, 1.23. Found: C, 44.19; H, 2.13; N, 1.11.

$[\{{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}\}_2(\mu\text{-Br})]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 6. To a solution of compound **3** (0.30 mmol, 342 mg) in 5 mL of CH_2Cl_2 was added a solution of bromide **1a** (0.30 mmol, 162 mg) in 6 mL of CH_2Cl_2. The reaction mixture was stirred at room temperature for 2 h, and the solvent was removed under vacuum to give compound **6** as a white solid. Recrystallization from CH_2Cl_2/hexane furnished compound **6** as colorless crystals containing CH_2Cl_2 (439 mg, 83%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 8.66 (dd, J = 7.5, 1.2 Hz, 4H), 7.66 (dd, J = 7.5, 0.8 Hz, 4H), 7.52 (td, J = 7.5, 1.4 Hz, 4H), 7.47 (td, J = 7.5, 1.3 Hz, 4H), 4.78 (d, J = 15.5 Hz, 4H), 4.44 (d, J = 15.5 Hz, 4H), 1.38 (s, 18H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 175.1, 153.7, 148.6 (d, J_{CF} = 240 Hz), 140.0, 138.7 (d, J_{CF} = 243 Hz), 136.7 (d, J_{CF} = 241 Hz), 131.9, 129.6, 128.7, 124.6 (bs), 62.95, 62.85, 28.1. IR (KBr): 2980, 1644, 1512, 1462, 1086, 980, 756 cm^{-1}. Anal. Calcd for $C_{60}H_{42}BBi_2BrF_{20}N_2\cdot CH_2Cl_2$: C, 41.52; H, 2.51; N, 1.59. Found: C, 41.47; H, 2.43; N, 1.57.

$[\{{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}\}_2(\mu\text{-Cl})]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 7. To a slurry of $\mathrm{Li}[\mathrm{B}(\mathrm{C_6F_5})_4]$ (0.50 mmol, 343 mg) in 5 mL of CH_2Cl_2 at −20 °C was added a cooled (−20 °C) solution of chloride **1b** (1.0 mmol, 496 mg) in 10 mL of CH_2Cl_2. The reaction mixture was stirred at −20 °C for 2 h and then allowed to warm slowly to room temperature. The precipitated LiCl was removed by filtration, and the solvent was removed under vacuum to give compound **7** as a white solid. Recrystallization from CH_2Cl_2/hexane furnished compound **7** as colorless crystals containing CH_2Cl_2 (735 mg, 85%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 8.57 (d, J = 7.5 Hz, 4H), 7.67 (d, J = 7.5 Hz, 4H), 7.55 (td, J = 7.5, 0.9 Hz, 4H), 7.46 (td, J = 7.5, 1.3 Hz, 4H), 4.80 (d, J = 15.5 Hz, 4H), 4.45 (d, J = 15.5 Hz, 4H), 1.39 (s, 18H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 176.7, 153.6, 148.6 (d, J_{CF} = 242 Hz), 138.8, 138.7 (d, J_{CF} = 243 Hz), 136.7 (d, J_{CF} = 245 Hz), 131.7, 129.5, 128.8, 124.6 (bs), 63.0, 62.8, 28.1. IR (KBr): 2980, 1643, 1512, 1462, 1086, 980, 754 cm^{-1}. Anal. Calcd for $C_{60}H_{42}BBi_2ClF_{20}N_2\cdot CH_2Cl_2$: C, 42.59; H, 2.58; N, 1.63; Cl, 6.18. Found: C, 42.52; H, 2.62; N, 1.61; Cl, 6.16.

$[\{{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}\}(\mathrm{MeCHO})]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 8. To a solution of compound **3** (0.50 mmol, 570 mg) in 5 mL of CH_2Cl_2 was added an excess of acetaldehyde (ca. 0.12 mL, 2 mmol). After the mixture was stirred at room temperature for 3 h, 10 mL of hexane was added and the mixture was cooled to −25 °C for 3 days to give complex **8** as colorless crystals (273 mg, 46%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 9.89 (q, J = 3.0 Hz, 1H), 7.96 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 4.94 (d, J = 15.5 Hz, 2H), 4.63 (d, J = 15.5 Hz, 2H), 2.44 (d, J = 3.0 Hz, 3H), 1.44 (s, 9H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 207.5, 182.2, 154.6, 148.6 (d, J_{CF} = 245 Hz), 138.7 (d, J_{CF} = 244 Hz), 137.4, 136.7 (d, J_{CF} = 244 Hz), 132.4, 130.1, 129.4, 124.1 (bs), 65.5, 64.8, 32.0, 28.4. IR (KBr): 2984, 1699 (C=O), 1645, 1516, 1464, 1090, 980 cm^{-1}. Anal. Calcd for $C_{44}H_{25}BBiF_{20}NO$: C, 44.66; H, 2.13; N, 1.18. Found: C, 44.41; H, 2.16; N, 1.19.

$[\{{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}\}(\mathrm{MeOH})]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 9. To a solution of compound **3** (0.20 mmol, 223 mg) in 2 mL of CH_2Cl_2 was added methanol (10 μL, 0.25 mmol). The reaction mixture was stirred at room temperature for 3 h, and then the solvent was removed under vacuum to give compound **9**. Recrystallization from CH_2Cl_2/hexane furnished compound **9** as colorless crystals (195 mg, 85%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 7.94 (d, J = 7.5 Hz, 2H), 7.78 (d, J = 7.5 Hz, 2H), 7.71 (t, J = 7.5 Hz, 2H), 7.51 (td, J = 7.5, 1.2 Hz, 2H), 4.92 (d, J = 15.5 Hz, 2H), 4.63 (d, J = 15.5 Hz, 2H), 3.78 (s, 3H), 2.68 (bs, OH), 1.42 (s, 9H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 182.0, 154.6, 148.6 (d, J_{CF} = 243 Hz), 138.7 (d, J_{CF} = 245 Hz), 137.1, 136.7 (d, J_{CF} = 244 Hz), 132.4, 130.3, 129.5, 124.1 (bs), 65.4, 64.7, 53.0, 28.4. IR (KBr): 3609 (OH), 2982, 1645, 1516, 1464, 1090, 980 cm^{-1}. Anal. Calcd for $C_{43}H_{25}BBiF_{20}NO$: C, 44.09; H, 2.15; N, 1.20. Found: C, 43.53; H, 2.18; N, 1.17.

$[\{{}^t\mathrm{BuN}(\mathrm{CH_2C_6H_4})_2\mathrm{Bi}\}(\mathrm{MeCN})]^+[\mathrm{B}(\mathrm{C_6F_5})_4]^-$, 10. To a solution of compound **3** (0.20 mmol, 223 mg) in 2 mL of CH_2Cl_2 was added acetonitrile (12.5 μL, 0.24 mmol). The reaction mixture was stirred at room temperature for 3 h, and then the solvent was removed under vacuum to give compound **10**. Recrystallization from CH_2Cl_2/hexane furnished compound **10** as colorless crystals (203 mg, 88%). ^{1}H NMR (499.1 MHz, CD_2Cl_2): δ 8.15 (d, J = 7.5 Hz, 2H), 7.73 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.5 Hz, 2H), 7.50 (t, J

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(56) Preliminary evaluation of the catalytic performance of the cationic complex **3** showed it worked as a Lewis acid catalyst for allylation reaction of aldehydes with allylbismuth species and the Mukaiyama aldol reaction.

= 7.5 Hz, 2H), 4.87 (d, J = 15.5 Hz, 2H), 4.53 (d, J = 15.5 Hz, 2H), 2.36 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (125.4 MHz, CD_2Cl_2): δ 180.1, 154.1, 148.6 (d, J_{CF} = 241 Hz), 138.7 (d, J_{CF} = 245 Hz), 137.7, 136.7 (d, J_{CF} = 241 Hz), 132.3, 130.0, 129.2, 124.5 (bs), 119.4, 64.6, 64.2, 28.3, 2.8. IR (KBr): 3061, 2984, 2267 (CN), 1644, 1514, 1464, 1086, 980 cm^{-1}. Anal. Calcd for $C_{44}H_{24}BBiF_{20}N_2$: C, 44.77; H, 2.05; N, 2.37. Found: C, 44.62; H, 2.04; N, 2.34.

$[\{^{t}BuN(CH_2C_6H_4)_2Bi\}(CH_2Cl_2)]^+[B(C_6F_5)_4]^-$, 11. To a solution of compound **3** (0.20 mmol, 223 mg) in 2 mL of CH_2Cl_2 was added Ph_2O (35 μL, 0.22 mmol) or Ph_2S (37 μL, 0.22 mmol). The reaction mixture was stirred at room temperature for 6 h, and then the mixture was cooled to −20 to −30 °C to give colorless crystals, which were proved to be complex **11** by single-crystal X-ray analysis.

X-ray Crystallography. Data collection was performed on a Bruker Smart Apex CCD diffractometer (Mo Kα radiation, graphite monochromator) except for complex **3**, for which a Rigaku AFC7R system (Mo Kα radiation, graphite monochromator) was used. Data were corrected for absorption. The structures were solved by the Patterson method. Structure refinement was carried out by full-matrix least-squares on F^2. The hydrogen atoms were placed in calculated positions and refined using a riding model. For complex **9**, the hydrogen atom bound to the methanol oxygen atom could not be located. Table 2 gives further details. Structure solution and refinement were performed using the CrystalStructure software package[57] with Crystals[58] and SHELX-97[59] programs. Ortep drawings were generated using the ORTEP-3 for windows program.[60] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (int.) +44-1223/336-033; e-mail, data_request@ccdc.cam.ac.uk), on quoting the deposition numbers CCDC-631261 (**3**), CCDC-631262 (**6**), CCDC-631263 (**7**), CCDC-631264 (**8**), CCDC-631265 (**9**), CCDC-631266 (**10**), and CCDC-631267 (**11**).

Acknowledgment. This work was partially supported by the Japan Society for the Promotion of Science (JSPS), and M.B. thanks the JSPS for a postdoctoral fellowship.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0611453

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