Synthesis, Structure, and Reactivity of Borate Ester Coordinated Organobismuth Compounds

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A new class of hypervalent organobismuth compounds functionalized with coordinating pinacolborate esters of the nature $ArBiCl_2$ (**2**), Ar_3Bi (**3**), $ArPh_2Bi$ (**4**), Ar_3BiCl_2 (**5**), and $ArPh_2BiCl_2$ (**6**), where Ar = 3-fluoro-2-pinacolatoboronphenyl, have been prepared and structurally characterized. The Bi···O distance is between 2.58 and 3.47 Å in the solid state for all compounds, and reasonable bonding interactions are presumed to exist in compounds **2**−**4** and **6**, where Bi···O < 3.0 Å. When $ArPh_2BiCl_2$ (**6**) is exposed to CsF in the presence of furan, the [4 + 2] cycloaddition product of 3-fluorobenzyne + furan, **8**, is isolated in 58% yield. Mechanistic evidence is offered to support the claim that **6** undergoes an unprecedented fluoride-promoted fragmentation to generate 3-fluorobenzyne, pinacol, BF_3, and Ph_2BiF.

Introduction

Organobismuth compounds have broad application in multiple areas of chemistry. They have medicinal value for the treatment of *H. pylori* infections and as antifungal agents.[1–3] Organobismuth reagents also have synthetic utility as coupling partners in numerous reactions,[4,5] including enolate arylations[6] and metal-catalyzed C−O[7] and C−N[8] bond-forming reactions.

Interest in bismuth chemistry has driven synthetic efforts in recent years to prepare organobismuth compounds with greater functional complexity.[9] Notable are the new classes of arylbismuth compounds that are stabilized by the intramolecular coordination of pendant Lewis bases.[10] Most of the compounds reported utilize chelating tertiary amines: for example $2\text{-}(Me_2NCH_2)C_6H_4-$,[11] $2\text{-}(Me_2N)C_{10}H_6-$,[12] and more recently the N,C,N pincer ligand $2,6\text{-}(Me_2NCH_2)_2C_6H_3-$.[13] Organobismuth compounds containing a chelating oxygen ether functionality are somewhat less common, and recent examples include the $2,6\text{-}(MeO)_2C_6H_3-$[14] and O,C,O pincer ligands $2,6\text{-}(ROCH_2)C_6H_3-$ (R = Me, ^{t}Bu).[15]

Our laboratory is interested in preparing organobismuth compounds that contain hypervalent stabilizing groups with complex functionalities to increase the diversity and ultimately the scope of organobismuth chemistry. We chose to prepare bismuth complexes containing a borate ester moiety because of their relative rarity as oxygen donors in coordination compounds and because of their importance in metal-catalyzed cross-coupling reactions.[16] We describe herein the synthesis of a new class of organobismuth compounds bearing the ligand 3-fluoro-2-pinacolatoboronphenyl. To our knowledge, this is the first example of an organobismuth compound that contains organic boron groups. We report both the X-ray structures and solution behavior of compounds **2**−**6**. Finally, we disclose an unprecedented fluoride-promoted fragmentation of the triarylbismuthane **6** to yield products consistent with the generation of 3-fluorobenzyne.

Results and Discussion

Preparation of Arylbismuthines 2–4. Compounds **2**−**4** were prepared by reacting Grignard reagent **1** with $BiCl_3$ or Ph_2BiCl at −78 °C, as depicted in Scheme 1.[17] After the mixtures were stirred overnight and warmed to room temperature, the desired arylbismuthines were isolated in low (**2**, 14%) to good (**3**, 60%; **4**, 65%) yield. Compounds **3** and **4** were purified by silica gel chromatography (hexanes/dichloromethane) followed by recrystallization (**3**, ethyl acetate/methanol; **4**, dichloromethane/methanol), to give colorless crystals suitable for X-ray diffraction. In the crystalline state, compounds **2**−**4** have been stored under air for several months without any noticeable decomposi-

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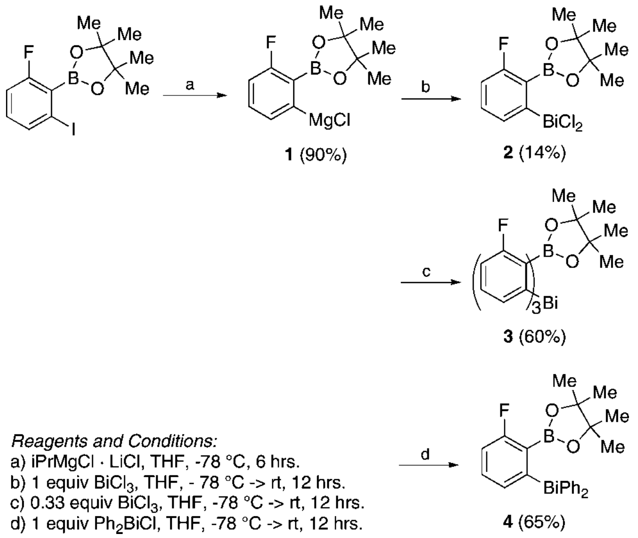
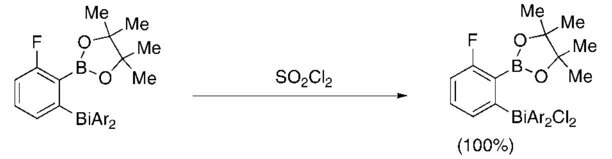
10.1021/om7009792 CCC: $40.75

Scheme 1



Reagents and Conditions:
a) iPrMgCl · LiCl, THF, -78 °C, 6 hrs.
b) 1 equiv $BiCl_3$, THF, - 78 °C -> rt, 12 hrs.
c) 0.33 equiv $BiCl_3$, THF, -78 °C -> rt, 12 hrs.
d) 1 equiv Ph_2BiCl, THF, -78 °C -> rt, 12 hrs.

Scheme 2



3: Ar = 3-fluoro-2-pinacolato-boronphenyl
4: Ar = phenyl

5: Ar = 3-fluoro-2-pinacolato-boronphenyl
6: Ar = phenyl

tion. Compound **2** has poor solubility in organic solvents, which contributed to the low isolated yield. Despite this limitation, a small quantity of colorless needles were collected from a solution of **2** in dichloromethane that were suitable for X-ray diffraction.

Preparation of Dichlorotriarylbismuthanes 5 and 6. Compounds **5** and **6** were prepared by respective treatment of **3** and **4** with an excess of freshly distilled sulfuryl chloride in benzene at ambient temperature (Scheme 2). Immediate solvent removal followed by NMR analysis (C_6D_6) showed quantitative conversion to the dichlorides **5** and **6** with no further purification necessary. X-ray-quality crystals were grown by slow infusion of pentane into concentrated benzene solutions of **5** and **6**. Compound **5** was stable in a solution of C_6D_6 at 4 °C over 4 days without decomposition, but both **5** and **6** showed appreciable decomposition in $CDCl_3$ within 4 h at room temperature.

Solid-State Structures of 2–6. The data collection and structural refinement parameters for crystals of **2**−**6** are summarized in Table 1. Select bond angles and distances for **2**−**6** are presented in Table 2.

Compound **2** crystallized in a square-pyramidal motif with an infinite chain of bridging chlorides (Figures 1 and 2). The Bi−O bond distance is 2.58 Å, which is well within the van der Waal radii of Bi and O (3.9 Å) and is similar to the Bi−O bond distance (2.50 Å) reported for the related complex [2,6-$(MeOCH_2)C_6H_3]BiCl_2$.[15] The Bi−Cl bond lengths varied depending on coordination geometry and measured 2.52 Å (Cl trans to Bi−O), 2.65 (Cl cis to Bi−O, bridging covalent), and 2.90 (bridging Bi−Cl, non-covalent).

Compound **3** crystallized in a pseudo-octahedral geometry with three pinacolborate ester oxygens coordinated to the bismuth center (Figure 3). The Bi−O average bond distance is 2.90 Å, still within the van der Waals radii of 3.9 Å and slightly shorter than the bond distances reported for similar structures with chelating $-NMe_2$ groups (2.97–3.15 Å).[11] The ^1H NMR spectrum of **3** at room temperature showed a broad doublet at 1.16 ppm corresponding to the pinacol methyl groups. When the temperature was raised to 55 °C, the doublet coalesced to a broad singlet. The ^1H NMR spectrum and coalesce temperature was not affected by changing the solvent to CD_3OD.

Organobismuth(III) complexes with intramolecularly coordinated −OR or $-NR_2$ functionalities rarely show magnetic inequivalence of their R groups in their NMR spectra.[18] The doublet observed for the pinacol methyl groups in the ^1H spectrum of **3** is likely due to restricted rotation about the C−B bond due to the steric bulk of three pinacolborane groups crowded around the central bismuth atom. A consequence of the rigidity of the C−B bond is that the borate oxygens are forced into an ideal conformation to coordinate the bismuth atom.

Compound **4** adopts an equatorially vacant trigonal-bipyramidal conformation in the solid state (Figure 4). **4** also showed structural properties very similar to those of **3**, including an almost identical Bi−O bond distance of 2.89 Å. The C−Bi−C′ bond angles of **4** have an average of 95.3°, in comparison to **3**, which has a slightly smaller C−Bi−C′ bond angle average of 92.8°. The larger C−Bi−C′ bond angles of **4** compared to **3** reflect the reduced steric effect of having only one bulky pinacolborane group in the ligand sphere.

Compound **5** crystallized in a trigonal-bipyramidal motif with one molecule of benzene in the asymmetric unit (Figure 5). The Bi···O distances varied widely from 3.2 to 3.47 Å, and the orientation of the pinacolborate oxygens is not ideal to form a Bi−O bond. Therefore, it is assumed very weak, if any, Bi···O bonding interactions are present in the solid state. The Cl(1)−Bi(1)−Cl(2) bond angle is bent noticeably from the ideal geometry of 180° to 169.7°. The bent Cl(1)−Bi(1)−Cl(2) angle is likely the result of steric pressure of two pinacolborane groups occupying the same face of the molecule, causing the chloride ligands to bend in the opposite direction. Compound **6**, a related compound with only one pinacolborane moiety, has a Cl(1)−Bi(1)−Cl(2) bond angle of 175.2°.

At low temperature (−50 °C) the ^1H NMR spectra of **5** showed an interesting dependence on solvent. In a nonpolar solvent, $CDCl_3$, two broad resonances were observed at 1.2 ppm corresponding to the pinacol methyl groups. When the temperature was raised, the peaks coalesced to a broad singlet at −20 °C and a sharp singlet at room temperature. Repetition of the experiment using a more polar solvent, CD_3OD, showed the pinacol methyl groups as a sharp singlet down to −80 °C. This observation supports the hypothesis that at low temperature solvation of the pinacolborane group by methanol suppresses intramolecular coordination of the pinacol oxygen atoms to the bismuth center.

Compound **6** crystallized with two independent molecules in the asymmetric unit (Figure 6). For both molecules the geometry was observed to be pseudooctahedral, with a pinacolborate oxygen occupying an equatorial coordination site. The Bi−O bond distance was 2.96 Å in both molecules, which is only a slight increase from the Bi−O bond distance of 2.89 Å in the precursor bismuthine **4**. The Cl(1,3)−Bi(1,2)−Cl(2,4) bond angles differed between the two X-ray structures and measured 175.2 and 172.4°. The C(1)−Bi(1)−C(13) bond angle is bent substantially to 146.0° to accommodate the coordinating pinacolborane group, which adopts a nearly planar configuration with the bismuth ligand framework.

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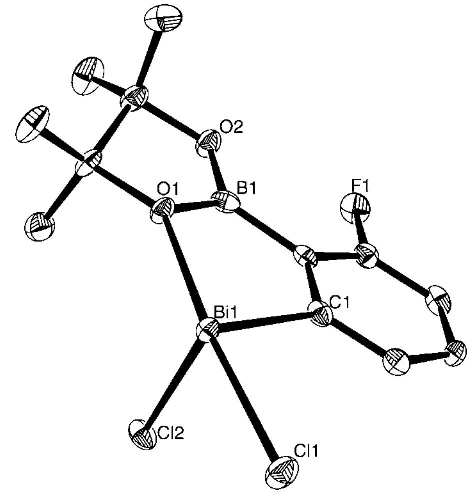

Figure 1. ORTEP plot of compound **2**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

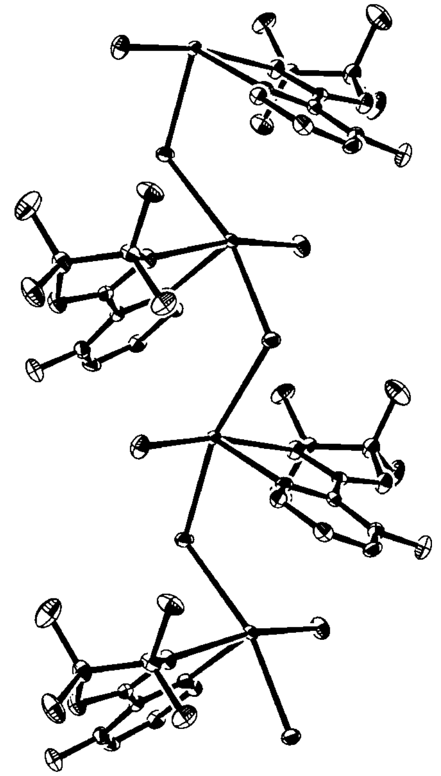

Figure 2. ORTEP plot of **2** showing infinite chloride-bridged chains in the crystal lattice. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Solid-State Analysis. Complexes **2**–**4** and **6** all showed Bi–O bond distances under 3.0 Å, which is between the covalent radii (2.16 Å) and van der Waals radii (3.9 Å) and consistent with the literature precedent for a Bi–O bonding interaction.[10] The structure of compound **5** did not support a reasonable likelihood of Bi–O bonding interactions, on the basis of long Bi···O distances between 3.2 and 3.47 Å.

The coordination of the chelating oxygen atoms showed a strong preference to orient trans to the Bi–C_{aryl} σ bonds. The measured O···Bi–C_{aryl} bond angles for complexes **2**–**4** and **6** were narrowly confined between 160.3 and 166.1°, whereas the O···Bi–C_{aryl} bond angles of complex **5** measured between 148.5 and 156.9°. The preference for oxygen coordination trans to the Bi–C_{aryl} σ bond can be attributed to donation of the oxygen lone pair into the Bi–C_{aryl} σ^* orbital.[19] Complex **5**, with the large steric bulk of three pinacolborates and two chlorides, cannot adopt the preferred trans confirmation to effectively overlap with the Bi–C_{aryl} σ^* orbital.

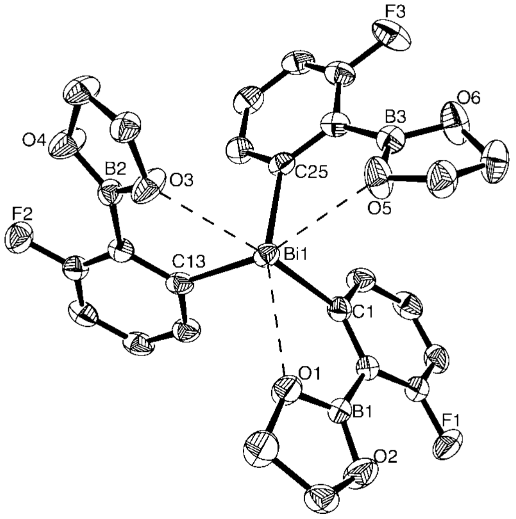

Figure 3. ORTEP plot of compound **3**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and pinacol methyl groups are omitted for clarity.

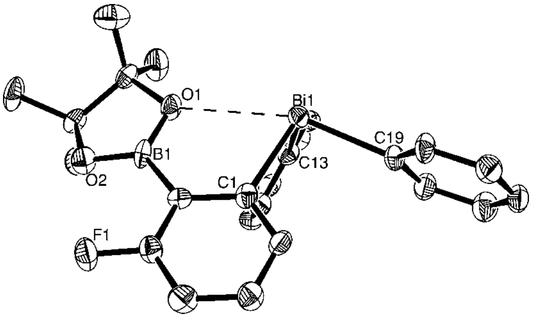

Figure 4. ORTEP plot of compound **4**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

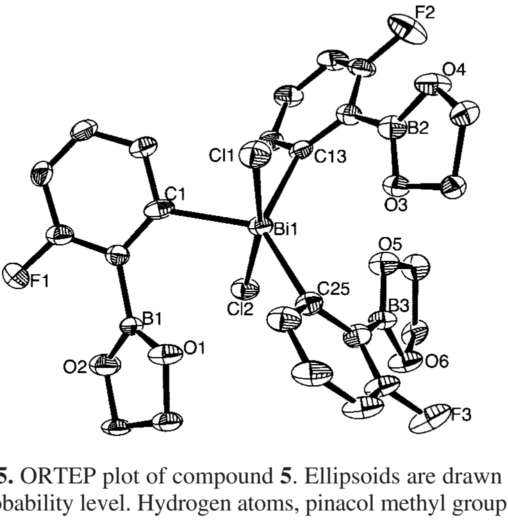

Figure 5. ORTEP plot of compound **5**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, pinacol methyl groups, and a benzene solvent molecule are omitted for clarity.

Fluoride-Promoted Disproportionation of 6. We sought to study the corresponding difluorotriarylbismuthanes of com-

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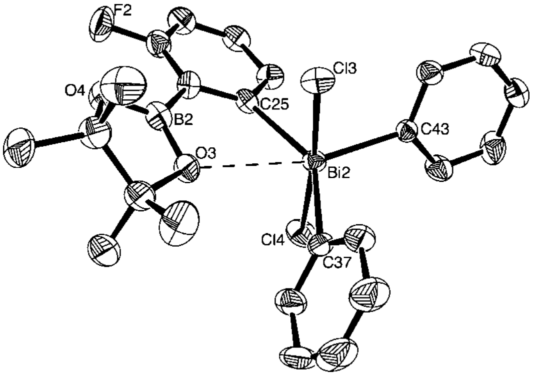


Figure 6. ORTEP plot of compound **6**. Only one of two of the independent molecules in the asymmetric unit are shown. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

pounds **5** and **6** to determine whether the boron atom would engage in a bridging bond to the bismuth-bound fluoride ligand (Figure 7).

Complexes with the ability to recognize and chelate fluoride are an important class of molecules used as fluoride sensors.[20] Bidentate complexes that rely on a mixed Lewis acid bridging B···F···L motif, where L = HgC_6F_5,[21] $HNC(O)CF_3$,[22] $B(Mes)_2$,[23] $B(C_6F_5)_2$[24] have been reported to have enhanced fluoride-binding properties. Since bismuth is known to be fluorophilic, these compounds have the potential to be high-affinity fluoride chelators.[3,25]

Treatment of **5** or **6** with 2 equiv of tetramethylammonium fluoride (TMAF) in methanol did not lead to the desired difluorobismuthane but instead resulted in rapid decomposition and formation of an off-white precipitate (Scheme 3).[26] Further analysis of the reaction mixture of **6** with excess TMAF in CD_3OD revealed that the deuterated arene **7** was formed in 75% yield as a single regioisomer, along with BF_3, pinacol, triphenylbismuthine, and an insoluble solid presumed to be inorganic bismuth salts.[27] The observed products are consistent with formation of 3-fluorobenzyne, which reacts with CD_3OD to give the expected regiochemical isomer.[28] The immediate side products of the reaction are pinacol, BF_3, and transiently formed Ph_2BiF, which undergoes a well-documented transmutation to give Ph_3Bi and inorganic bismuth salts.[29]

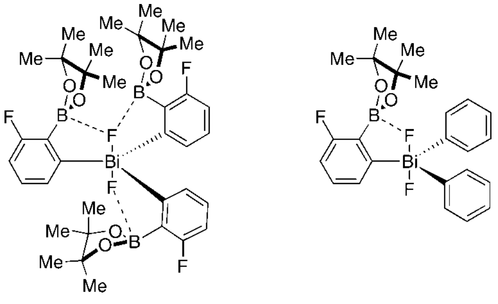
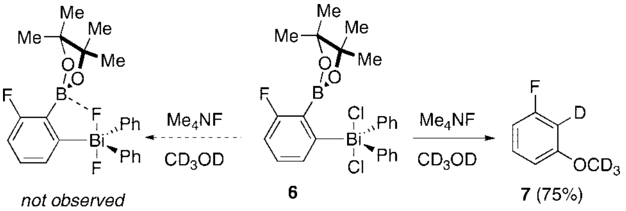
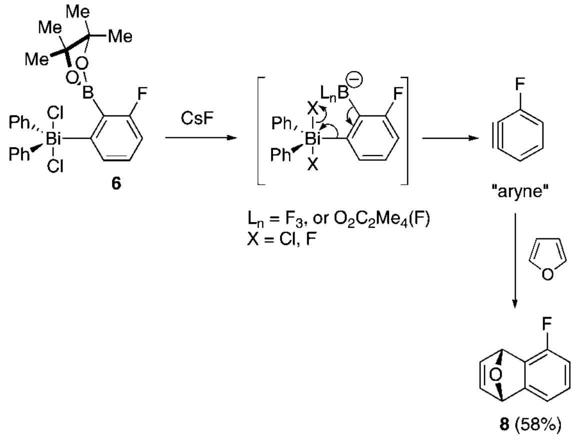


Figure 7. Hypothetical B···F···Bi bidentate mixed Lewis acid complexes.

Scheme 3



Scheme 4



Since arynes are known to undergo [4 + 2] cycloadditions, **6** was treated with excess CsF in furan to further validate the hypothesis that 3-fluorobenzyne is generated under the reaction conditions.[30] After 4 h the reaction mixture was concentrated *in vacuo* and chromatographed to yield cycloadduct **8** in 58% yield (Scheme 4). On the basis of this preliminary evidence, we theorize that fluoride displaces the pinacol ester to give the trifluoroborate salt. This intermediate eliminates to give a highly reactive "aryne", which then undergoes the [4 + 2] cycloaddition with furan to give the observed product.[31] The fluoride-promoted reactions of **6** with CD_3OD and furan are the first examples of organobismuth compounds being used as precursors to generate benzyne equivalents.

Conclusion

We have described the synthesis and structure of a new class of organobismuth compounds that contain intramolecularly coordinated pinacolborate esters. Probing the reactivity of these compounds, we discovered a mild method to generate arynes using anionic fluoride at ambient temperature. The use of organobismuth compounds as benzyne precursors is shown as a selective way to generate arynes that are viable as coupling partners in both [4 + 2] cycloadditions and the addition of

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(26) Attempts to prepare **5** or **6** directly by oxidizing **3** or **4** with XeF_2 were unsuccessful. Control experiments demonstrated that XeF_2 is incompatible with the borate functionality.

(27) The yield for **7** was based on GC analysis using methanol with 4-bromoanisole as the internal standard. BF_3, pinacol, and triphenylbismuthine were all identified by comparison of their ^1H, ^{19}F, or ^{11}B spectra to those of authentic samples.

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Table 1. Crystal Data Collection and Refinement Parameters for Compounds 2–6

	2	**3**	**4**	**5**	**6**
chem formula	$C_{12}H_{15}BBiCl_2FO_2$	$C_{36}H_{45}B_3BiF_3O_6$	$C_{24}H_{25}BBiFO_2$	$C_{42}H_{51}B_3BiCl_2F_3O_6$	$C_{24}H_{25}BBiCl_2FO_2$
formula wt	500.93	872.13	584.23	1021.14	655.13
cryst habit	colorless, needle	colorless, block	colorless, rod	colorless, plate	colorless, block
cryst size (mm)	0.40 × 0.05 × 0.05	0.35 × 0.35 × 0.25	0.40 × 0.13 × 0.10	0.25 × 0.25 × 0.08	0.25 × 0.15 × 0.05
T (K)	123(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	orthorhombic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a (Å)	9.1514(7)	11.6453(9)	10.399(3)	15.0270(16)	9.4733(6)
b (Å)	11.6274(9)	13.4108(10)	10.701(3)	24.892(3)	13.9288(8)
c (Å)	14.5092(11)	24.5109(18)	11.484(3)	11.7187(12)	37.941(2)
α (deg)	90	90	94.046(4)	90	90
β (deg)	90	94.0630(10)	95.697(4)	93.247(2)	90
γ (deg)	90	90	118.484(3)	90	90
U (Å^3)	1543.9(2)	3818.3(5)	1107.6(5)	4376.4(8)	5006.4(5)
Z	4	4	2	4	8
D_c (g cm^{-3})	2.155	1.517	1.752	1.55	1.738
abs coeff (mm^{-1})	11.769	4.673	7.984	4.208	7.282
F(000)	936	1736	564	2040	2528
θ range (deg)	2.24–27.49	1.67–27.50	1.80–25.11	1.36–25.68	1.56–27.50
no. of rflns measd	18 062	43 874	3928	38 227	59 270
no. of unique rflns	3525	8708	3928	8324	11 417
R_{int}	0.0425	0.0348	0.0425	0.105	0.0517
R1[a] ($I > 2\sigma(I)$)	0.0183	0.0245	0.0352	0.0592	0.0263
wR2[b] (F^2, all rflns)	0.0345	0.0589	0.087	0.1001	0.0526
no. of params	176	475	267	527	567
no. of restraints	0	32	0	12	0
S[c]	0.903	1.009	1.016	1.089	1.023
max, min $\Delta\rho$ (e Å^{-3})	0.724, −0.595	1.017, −0.527	1.459, −1.944	1.395, −0.857	1.233, −0.966

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (w_1P)^2 + w_2P]$, where $P = [2F_c^2 + \mathrm{Max}(F_o^2)]/3$. [c] GOF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

methanol. We expect that this new method of generating arynes will prove useful in organic synthesis.

Experimental Section

General Procedures. All reagents were obtained commercially at the highest available purity unless otherwise noted. All organometallic reactions were performed using oven-dried glassware under an inert atmosphere of argon using standard Schlenk line techniques. Dichloromethane, tetrahydrofuran (THF), and benzene were passed through two columns of activated alumina immediately prior to use. Sulfuryl chloride and furan were distilled from CaH_2 immediately prior to use. Chromatographic purification of products was accomplished using forced flow chromatography on Silicycle silica gel 60 (40–63 μm). Thin-layer chromatography was performed on EM Science silica gel 60 F_{254} plates (250 μm). Unless otherwise stated, nuclear magnetic resonance (NMR) spectra were acquired on a Varian GX-400 spectrometer and are referenced internally (^{1}H, ^{13}C) according to residual solvent signals or externally (^{19}F) to neat trifluoroacetic acid (−78.5 ppm). Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. Diphenylbismuth(III) chloride was prepared according to a literature procedure.[29]

2-(2-Fluoro-6-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. 2-Fluoro-6-iodophenylboronic acid (1.5 g, 5.64 mmol) was dissolved in 13 mL of toluene. Pinacol (666 mg, 5.64 mmol) was added to the solution and stirred until dissolved. A reflux condenser was attached to the reaction flask and the solution heated to reflux for 1 h. After 1 h the toluene was distilled away from the reaction mixture, facilitating the removal of water. The crude solid was purified by silica gel column chromatography (10% dichloromethane/90% hexanes) to yield the desired product as a white crystalline solid (1.431 g, 4.17 mmol, 73% yield). Anal. Calcd for $C_{12}H_{15}BFIO_2$: C, 41.62; H 4.58. Found: C, 41.42; H, 4.35. ^{1}H NMR ($CDCl_3$): δ 7.54 (ddd, 1H, 7.4 Hz, 1.3 Hz, 0.4 Hz), 6.9–7.1 (m, 2H), 1.4 (s, 12 H). ^{19}F NMR: δ −102.1 (dd, 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ 166.0, 163.54, 134.20, 134.21, 132.30, 132.21, 114.40, 114.17, 98.18, 98.09, 84.93, 24.79.

Synthesis of $[3\text{-F-2-BO}_2\text{C}_2(\text{CH}_3)_4]\text{BiCl}_2$ (2). 2-(2-Fluoro-6-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (200 mg, 0.575 mmol) was dissolved in 2 mL of THF and cooled to −78 °C using a dry ice/ethanol bath. To this solution was added dropwise isopropylmagnesium chloride·LiCl (1 M THF, 0.575 mL, 0.575 mmol). The reaction was monitored by GC/MS until complete conversion of the starting material to the Grignard reagent (5 h). A solution of $BiCl_3$ (145 mg, 0.460 mmol) in 2 mL of THF was cooled to −78 °C and transferred via cannula to the reaction flask, followed by two rinses of 1 mL of THF. The reaction mixture was stirred for 12 h and the bath warmed to room temperature. Upon completion the reaction mixture was poured into saturated NH_4Cl(aq) and extracted three times with EtOAc. The organic layer was washed with brine and then dried over Na_2SO_4. The organic layer was filtered and concentrated in vacuo to give an orange semisolid. The residue was recrystallized from dichloromethane to yield a small amount of white needles (33 mg, 0.066 mmol, 14% yield). Anal. Calcd for $C_{12}H_{15}BBiCl_2FO_2$: C, 29.02; H 3.21. Found: C, 28.77; H, 3.02. ^{1}H NMR (DMSO-d_6): δ 9.21 (d, 7.4 Hz, 1H, Ar H), 8.23 (m, 1H, Ar H), 7.19 (dd, 8.8 Hz, 7.4 Hz, 1H, Ar H) 1.36 (s, 12H). ^{19}F NMR: δ −100.7 (dd, 8.4 Hz). A satisfactory ^{13}C spectrum was not obtained due to the small amount of material formed from the reaction.

Synthesis of $[3\text{-F-2-BO}_2\text{C}_2(\text{CH}_3)_4]_3\text{Bi}$ (3). A procedure related to that used to make compound **2** was used, with 2-(2-fluoro-6-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (308 mg, 0.885 mmol), and isopropylmagnesium chloride·LiCl (1 M THF, 0.885 mL, 0.885 mmol) in 3 mL of THF. Then $BiCl_3$ (74 mg, 0.236 mmol) in 2 mL of THF was added. Upon completion the reaction mixture was concentrated in vacuo. The solid residue was suspended in toluene and filtered through Celite. The resulting residue was purified by silica gel chromatography (2% diethyl ether/98% toluene) followed by recrystallization (EtOAc/MeOH) to give X-ray-quality white crystals (120 mg, 0.140 mmol, 60% yield). Anal. Calcd for $C_{36}H_{45}B_3BiF_3O_6$: C, 49.70; H 5.39. Found: C, 49.58; H, 5.20. ^{1}H NMR ($CDCl_3$): δ 7.55 (d, 7.3 Hz, 3H, Ar H), 7.24 (m,

Table 2. Select Bond Distances and Angles for Compounds 2–6

Compound **2**			
Bi(1)−C(1)	2.266(4)	Bi(1)−Cl(2)	2.6543(9)
Bi(1)−Cl(1)	2.5194(9)	Bi(1)−Cl(2)#1	2.8983(10)
Bi(1)−O(1)	2.582(3)	Cl(2)−Bi(1)#2	2.8983(9)
C(1)−Bi(1)−Cl(1)	93.86(10)	O(1)−Bi(1)−Cl(2)	83.27(6)
C(1)−Bi(1)−O(1)	73.66(12)	C(1)−Bi(1)−Cl(2)#1	79.52(10)
Cl(1)−Bi(1)−O(1)	166.13(7)	Cl(1)−Bi(1)−Cl(2)#1	92.72(3)
C(1)−Bi(1)−Cl(2)	85.23(10)	O(1)−Bi(1)−Cl(2)#1	90.94(6)
Cl(1)−Bi(1)−Cl(2)	89.79(3)	Cl(2)−Bi(1)−Cl(2)#1	164.68(2)
Compound **3**			
Bi(1)−C(13)	2.293(3)	Bi(1)−O(3)	2.887(2)
Bi(1)−C(1)	2.300(3)	Bi(1)−O(5)	2.918(3)
Bi(1)−C(25)	2.310(3)	Bi(1)−O(1)	2.924(2)
C(13)−Bi(1)−C(1)	95.50(11)	O(5)−Bi(1)−O(1)	104.47(8)
C(13)−Bi(1)−C(25)	91.80(11)	C(1)−Bi(1)−O(1)	69.54(9)
C(1)−Bi(1)−C(25)	91.13(11)	C(25)−Bi(1)−O(5)	69.70(10)
O(3)−Bi(1)−O(5)	104.31(10)	C(13)−Bi(1)−O(3)	70.16(9)
O(3)−Bi(1)−O(1)	115.79(7)		
Compound **4**			
Bi(1)−C(13)	2.247(8)	Bi(1)−C(19)	2.285(7)
Bi(1)−C(1)	2.270(8)	Bi(1)−O(1)	2.885(5)
C(13)−Bi(1)−C(1)	95.5(3)	C(1)−Bi(1)−C(19)	94.4(3)
C(13)−Bi(1)−C(19)	96.0(3)	C(1)−Bi(1)−O(1)	70.2(2)
Compound **5**			
Bi(1)−C(25)	2.225(8)	Bi(1)−Cl(1)	2.597(2)
Bi(1)−C(13)	2.236(7)	Bi(1)−O(3)	3.197
Bi(1)−C(1)	2.242(8)	Bi(1)−O(5)	3.257
Bi(1)−Cl(2)	2.5919(19)	Bi(1)−O(1)	3.469
C(25)−Bi(1)−C(13)	128.5(3)	C(1)−Bi(1)−O(1)	63.84
C(25)−Bi(1)−C(1)	127.4(3)	C(25)−Bi(1)−O(5)	68.42
C(13)−Bi(1)−C(1)	104.1(3)	C(13)−Bi(1)−O(3)	67.17
Cl(2)−Bi(1)−Cl(1)	169.77(7)		
Compound **6**			
Bi(1)−C(13)	2.209(4)	Bi(2)−C(37)	2.197(5)
Bi(1)−C(19)	2.224(5)	Bi(2)−C(25)	2.214(5)
Bi(1)−C(1)	2.229(4)	Bi(2)−C(43)	2.223(5)
Bi(1)−Cl(1)	2.5841(13)	Bi(2)−Cl(3)	2.5832(12)
Bi(1)−Cl(2)	2.5973(12)	Bi(2)−Cl(4)	2.6009(14)
Bi(1)−O(1)	2.966(3)	Bi(2)−O(2)	2.967(3)
C(13)−Bi(1)−C(19)	109.58(16)	C(37)−Bi(2)−C(25)	141.48(18)
C(13)−Bi(1)−C(1)	145.67(17)	C(37)−Bi(2)−C(43)	111.49(18)
C(19)−Bi(1)−C(1)	104.75(17)	C(25)−Bi(2)−C(43)	107.03(17)
Cl(1)−Bi(1)−Cl(2)	172.42(4)	Cl(3)−Bi(2)−Cl(4)	175.20(5)
C(1)−Bi(1)−O(1)	68.43	C(25)−Bi(2)−O(3)	69.05

3H, Ar H), 7.19 (dd, 8.9 Hz, 7.3 Hz, 3H, Ar H), 1.21 (br s, 18H), 1.12 (br s, 18H). ^{19}F NMR: δ −101.8 (dd, 8.9 Hz, 3.8 Hz). ^{13}C NMR (C_6D_6): δ 182.06, 171.89, 169.34, 136.45, 136.38, 136.32, 136.29, 127.77, 114.39, 114.15, 84.09, 25.02, 24.71.

Synthesis of [3-F-2-$BO_2C_2(CH_3)_4$]$BiPh_2$ (4). A procedure related to that used to make compound **3** was used, with 2-(2-fluoro-6-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (500 mg, 1.46 mmol) and isopropylmagnesium chloride·LiCl (0.95 M THF, 1.53 mL, 1.46 mmol) in 3.5 mL of THF. Then diphenylbismuth(III) chloride (465 mg, 1.17 mmol) in 3 mL of THF was added. The resulting residue was purified by silica gel chromatography (3% EtOAc/97% hexanes) followed by recrystallization (dichloromethane/MeOH) at −20 °C to give X-ray-quality white crystals (444 mg, 0.760 mmol, 65% yield). Anal. Calcd for $C_{24}H_{25}BBiFO_2$: C, 49.20; H 4.52. Found: C, 49.34; H, 4.31. ^{1}H NMR ($CDCl_3$): δ 7.73 (dd, 7.8 Hz, 1.4 Hz, 4H, Ar H), 7.55 (ddd, 7.3 Hz, 0.95 Hz, 0.6 Hz, 1H, Ar H), 7.27–7.39 (m, 7H, Ar H), 6.96 (ddd, 9.7 Hz, 8.2 Hz, 0.95 Hz, 1H, Ar H), 1.17 (s, 12H). ^{19}F NMR: δ −100.8 (dd, 9.7 Hz, 5.8 Hz). ^{13}C NMR (C_6D_6): δ 171.95, 169.40, 169.24, 162.09, 138.07, 136.13, 136.06, 135.36, 135.33, 130.79, 127.66, 115.15, 114.90, 84.21, 24.74.

Synthesis of [3-F-2-$BO_2C_2(CH_3)_4$]$_3BiCl_2$ (5). Compound **3** (25 mg, 0.027 mmol) was dissolved in 3 mL of benzene. Freshly distilled SO_2Cl_2 was added (3.5 μL, 0.041 mmol) and the reaction mixture immediately concentrated in vacuo. The residue was further dried for 1 h at 0.5 mmHg to ensure complete removal of SO_2Cl_2. The desired product was obtained in quantitative yield. X-ray-quality crystals were obtained by vapor infusion of pentane into a concentrated solution in benzene. ^{1}H NMR (C_6D_6): δ 8.13 (br d, 8.0 Hz, 3H, Ar H), 6.91 (ddd, 8.6 Hz, 8.1 Hz, 5.2 Hz, 3H, Ar H), 6.68 (dd, 8.6 Hz, 3H, Ar H), 1.01 (s, 36H). ^{19}F NMR: δ −97.0 (br s). ^{13}C NMR (C_6D_6): δ 173.99, 169.85, 167.80, 133.20, 133.14, 131.64, 128.53, 128.29, 124.13, 117.60, 117.40, 85.04, 25.02. An accurate elemental analysis could not be obtained, due to the difficulty of removing trace solvent from the crystalline material.

Synthesis of [3-F-2-$BO_2C_2(CH_3)_4$]Ph_2BiCl_2 (6). A procedure related to that used to make compound **5** was used, with compound **4** (25 mg, 0.043 mmol) and SO_2Cl_2 (5 μL, 0.062 mmol) in 3 mL of benzene. The desired compound was isolated in quantitative yield. X-ray-quality crystals were obtained by vapor infusion of pentane into a concentrated solution in benzene. Anal. Calcd for $C_{24}H_{25}BBiCl_2FO_2$: C, 44.18; H 4.02. Found: C, 44.00; H, 3.85. ^{1}H NMR (C_6D_6): δ 8.92 (d, 7.8 Hz, 4H, Ar H), 7.60 (d, 7.9 Hz, 1H, Ar H), 7.19 (m, 4H, Ar H), 6.96 (t, 7.3 Hz, 2H, Ar H), 6.74 (ddd, 8.6 Hz, 7.9 Hz, 5.2 Hz, 1H, Ar H), 6.51 (dd, 8.6 Hz, 1H, Ar H), 1.0 (s, 12H). ^{19}F NMR: δ −94.37 (dd, 8.6 Hz, 5.2 Hz). ^{13}C NMR (C_6D_6): δ 175.52, 175.43, 170.32, 168.23, 135.86, 135.79, 134.88, 131.59, 131.04, 128.53, 128.29, 126.55, 126.52, 118.03, 117.83, 86.00, 24.20.

5-Fluoro-1,4-dihydro-1,4-epoxynaphthalene (8). Compound **6** (60.8 mg, 0.093 mmol) was dissolved in freshly distilled furan (3 mL). Flame-dried CsF (67 mg, 0.441 mmol) was added in one portion and the reaction mixture stirred for 4 h. Upon completion a large amount of white precipitate was present. The reaction mixture was partitioned between ethyl acetate and H_2O and the aqueous layer washed twice with ethyl acetate. The organic layers were combined, washed once with brine, and dried over Na_2SO_4. The drying agent was filtered off and the clear solution concentrated in vacuo and purified by SiO_2 chromatography (100% hexanes to 5% diethyl ether/95% hexanes). The desired product was isolated as a colorless residue (8.8 mg, 59% yield). The NMR spectra were identical with that of the previously reported compound.[31]

X-ray Crystallography. The structural and refinement data for compounds **2**−**6** are given in Table 1. A suitable crystal was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART Platform CCD diffractometer for data collection using monochromated Mo Kα radiation (λ = 0.710 73 Å) at 173(2) K. The intensity data were corrected for absorption and decay (SADABS).[32] The structures were solved by direct methods using SHELXS-97 and refined by SHELXL-97.[33] Full-matrix least-squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

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Supporting Information Available: CIF files giving crystallographic data for compounds **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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