Synthesis, Structure, and Reactions of Triaryl(methyl)bismuthonium Salts

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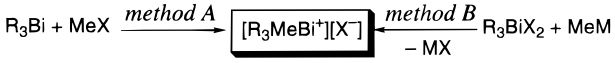
Treatment of triarylbismuth difluorides **2** (Ar_3BiF_2; **a**, Ar = Ph; **b**, Ar = 4-MeC_6H_4; **c**, Ar = 4-$MeOC_6H_4$; **d**, Ar = 2-$MeOC_6H_4$) with methylboronic acid (**3**) in the presence of BF_3·OEt_2 in CH_2Cl_2 afforded the corresponding triaryl(methyl)bismuthonium tetrafluoroborates **4a**−**d** ($[Ar_3MeBi^+][BF_4^-]$) in 42−91% yield. X-ray crystallographic analysis of compound **4d** revealed that the bismuth center possesses a distorted tetrahedral geometry with C−Bi−C bond angles of 106.1(3)−113.6(3)° and Bi−C bond lengths of 2.182(7)−2.195(8) Å. Compound **4a** transferred the methyl group to Ph_3E (E = P, As, Sb), tris(4-methylphenyl)bismuthine, ROH (R = Me, Et, *i*-Pr, $PhCH_2$), water, sodium benzenesulfinate, sodium benzoate, *N*,*N*-dimethylformamide (DMF), and thioacetamide to give the corresponding methylated products with a good recovery of triphenylbismuthine. The pseudo-first-order rate constant (k_{obsd} = 2.9×10^{-4} s^{-1}) observed for the reaction between **4a** and benzyl alcohol (**5d**) was about twice as large as that (k_{obsd} = 1.3×10^{-4} s^{-1}) between MeOTf and **5d** (in $CDCl_3$ at 23 °C; [**4a**] or [MeOTf] = 0.062 M; [**5d**] = 0.97 M). The observed reactivity of **4a** clearly demonstrates the high nucleofugality of the triphenylbismuthonio group.

Introduction

Methylated onium salts of the general formula $[R_nMeE^+][X^-]$ (E = group 15 and 16 elements; X^- = counteranion) have attracted considerable attention because of their importance in organic synthesis.[1] The reactivity of these onium salts differs considerably depending on the nature of the central element. However, very little information is available concerning methylbismuthonium salts ($[R_3MeBi^+][X^-]$) due to the limited access to this class of compounds.[2] As shown in Scheme 1, there are two possible methods for the synthesis of the methylbismuthonium salts: addition of a methyl cation equivalent to a triorganylbismuthine (method A) and metathesis of a methyl anion equivalent to a triorganylbismuth dihalide (method B). In 1994, Wallenhauer and Seppelt prepared tetramethylbismuthonium triflate by treating trimethylbismuthine with methyl triflate in acetonitrile.[3] In contrast, an earlier attempt by Henry and Wittig to prepare a methyltriphenylbismuthonium salt by the reaction of triphenylbismuthine with trimethyloxonium tetrafluoroborate[4] ($[Me_3O^+][BF_4^-]$) in liquid sulfur dioxide was unsuccessful.[5] Thus, method A has been applicable only to the synthesis of the tetramethylbismuthonium salt. Nevertheless, no attention has been paid to method B thus far. For practical use, triaryl(methyl)bismuthonium salts are preferable substrates because triarylbismuthines that would be produced in their reactions are much easier to handle than air-sensitive trimethylbismuthine.[6] Recently, the metathesis of triarylbismuth difluorides with organometallic reagents has proven to be a reliable method for the synthesis of various types of alkyltriarylbismuthonium salts.[7] Encouraged by these

Scheme 1



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(1) For monographs and reviews, see: (a) Johnson, A. W. *Ylides and Imines of Phosphorus*; Wiley: New York, 1993. (b) Lloyd, D.; Gosney, I.; Ormiston, R. A. *Chem. Soc. Rev.* **1987**, *16*, 45. (c) Lloyd, D.; Gosney, I. In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; Patai, S., Ed.; Wiley: New York, 1994; Chapter 16, pp 657−693. (d) Trost, B. M.; Melvin, L. S., Jr. *Sulfur Ylides*; Academic Press: New York, 1975. (e) Johnson, C. R. *Acc. Chem. Res.* **1973**, *6*, 341. (f) Johnson, A. W. *Ylide Chemistry*; Academic Press: New York, 1966.

(2) Arbuzov et al. postulated the formation of an intermediary methyltriphenylbismuth cation in the reaction between triphenylbismuthine and a sulfonium ylide. However, their attempt to isolate a methyltriphenylbismuthonium salt was not successful. Arbuzov, B. A.; Belkin, Y. V.; Polezhaeva, N. A.; Buslaeva, G. E. *Izv. Akad. Nauk SSSR* **1978**, 1643.

(3) Wallenhauer, S.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 976.

(4) Meerwein, H.; Hinz, G.; Hofmann, P.; Kroning, E.; Pfeil, E. *J. Prakt. Chem.* **1937**, *147*, 257.

(5) Henry, M. C.; Wittig, G. *J. Am. Chem. Soc.* **1960**, *82*, 563. The authors reported that triphenylbismuthine reacts with the oxonium salt but does not produce a bismuthonium salt. They also reported that triphenylstibine reacts readily with the same oxonium salt to yield methyltriphenylstibonium tetrafluoroborate.

(6) (a) *Gmelin Handbuch der Anorganischen Chemie, Bismut-Organische Verbindungen*; Wieber, M., Ed.; Springer-Verlag: Berlin, l977; Band 47. (b) Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982**, *82*, 15.

(7) (a) Matano, Y.; Azuma, N.; Suzuki, H. *Tetrahedron Lett.* **1993**, *34*, 8457. (b) Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1739. (c) Matano, Y.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1995**, 2543. (d) Matano, Y.; Yoshimune, M.; Suzuki, H. *Tetrahedron Lett.* **1995**, *36*, 7475. (e) Matano, Y.; Yoshimune, M.; Azuma, N.; Suzuki, H. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1971. (f) Matano, Y.; Suzuki, H. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2673. (g) Matano, Y.; Rahman, M. M.; Yoshimune, M.; Suzuki, H. *J. Org. Chem.* **1999**, *64*, 6924.

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results, I aimed to prepare triaryl(methyl)bismuthonium salts based on method B and to elucidate their reactivity.

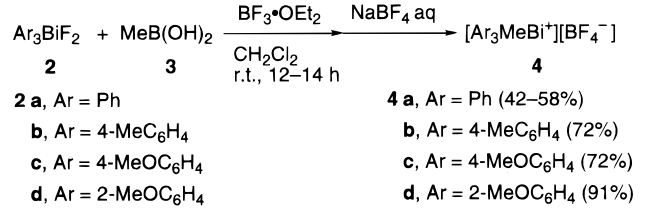
Reported here are the synthesis, structure, and reactions of triaryl(methyl)bismuthonium salts. The BF_3·OEt_2-promoted reaction of triarylbismuth difluorides with methylboronic acid has been found to be effective for constructing the Bi(V)−Me bond. Methyltriphenylbismuthonium tetrafluoroborate behaves as the methyl cation equivalent due to the remarkable nucleofugality of the triphenylbismuthonio group.

Results and Discussion

Synthesis of Triaryl(methyl)bismuthonium Salts. First, to confirm the earlier observation by Henry and Wittig,[5] the reaction of triphenylbismuthine (**1a**) together with the trimethyloxonium salt was reexamined. Treatment of **1a** with $[Me_3O^+][BF_4^-]$ in CH_2Cl_2/CH_3CN at room temperature afforded a significant amount of insoluble substance with *N*-methylacetamide[8] (ca. 80%), benzene,[9] and a small amount of unassigned bismuth compound.[10] As reported by Henry and Wittig, the desired methyltriphenylbismuthonium salt was not formed at all. The combined use of methyl iodide and silver tetrafluoroborate instead of $[Me_3O^+][BF_4^-]$ gave a similar result. Methyl triflate also did not transfer a methyl group to bismuthine **1a** after 1 week in $CDCl_3$ or in acetonitrile at room temperature. The observed reactivity of bismuthine **1a** is in marked contrast to those of Ph_3E (E = P, As, Sb), which readily react with $[Me_3O^+][BF_4^-]$ under similar conditions to yield the corresponding methylated onium salts, $[Ph_3MeE^+][BF_4^-]$.[5,11] Thus, methyltriphenylbismuthonium salts are much more difficult to prepare by method A than the lighter pnictogen counterparts. Apparently, this is due to the low nucleophilicity of the lone electron pair of triphenylbismuthine **1a**.[12]

Next, method B was examined using methylboronic acid as the methyl anion equivalent.[13] As shown in Scheme 2, treatment of triphenylbismuth difluoride (**2a**) with an excess of methylboronic acid (**3**) in the presence of BF_3·OEt_2 in CH_2Cl_2 at room temperature for 12 h afforded a mixture of methyltriphenylbismuthonium tetrafluoroborate (**4a**), difluoride **2a**, and a trace amount of tetraphenylbismuthonium tetrafluoroborate. The desired product **4a** usually was isolated in 42−58% yields by fractional recrystallization from CH_2Cl_2/Et_2O. Difluoride **2a** also was recovered in 30−40% yields. The formation of the tetraphenylbismuthonium salt could not be suppressed completely, and its yield increased with increasing reaction time.[14] Difluoride **2a** did not react with **3** in the absence of BF_3·OEt_2, and triphenylbismuth *dichloride* did not react with **3** even in the presence of BF_3·OEt_2. Presumably, BF_3 enhances the electrophilicity of the bismuth(V) center of **2a** by coordinating to the apical fluorine atom. Substituted triarylbismuth difluorides **2b**−**d** similarly underwent the BF_3·OEt_2-promoted reaction with **3** to afford the corresponding triaryl(methyl)bismuthonium tetrafluoroborates **4b**−**d** in 72−91% yields (Scheme 2). To the best of my knowledge, this is the first use of the boronic acid **3** in the synthesis of methylated onium salts.[15]

Scheme 2



Compounds **4** were characterized by ^1H NMR, IR, and MS spectroscopy as well as by elemental analysis. In the ^1H NMR spectra (in $CDCl_3$), the methyl group bound to the bismuth was observed at δ 3.17−3.29. The FABMS spectra of compounds **4** showed a strong fragment peak due to the $[M^+ - BF_4]$ cation, and their IR spectra showed a broad absorption due to the BF_4^- anion. These spectral data are consistent with the onium nature of the bismuth center in **4**. These compounds are soluble in $CHCl_3$, CH_2Cl_2, and CH_3CN, but insoluble in Et_2O and toluene. When kept in open air, compounds **4** gradually were hydrolyzed by atmospheric moisture. Under a dry condition or in dry $CDCl_3$, however, they did not decompose over a month.

The structure of **4d** was further elucidated by X-ray crystallographic analysis. The crystal data and collection parameters are given in Table 1, and an ORTEP diagram is shown in Figure 1 with selected bond lengths and angles. The bismuth center in **4d** possesses a distorted tetrahedral geometry with C−Bi−C bond angles of 106.1(3)−113.6(3)°. The Bi−C(1) bond length of 2.195(8) Å and the Bi−C_{Ar} bond lengths of 2.182(7)−2.189(7) Å in **4d** are almost identical with the reported values for the Bi−C_{Me} bonds of $[Me_4Bi^+][OTf^-]$[3] [2.210(7)−2.230(10) Å] and the Bi−C_{Ar} bonds of $[(2\text{-}MeOC_6H_4)_4Bi^+][Br^-]$[16] [2.194(8)−2.207(9) Å]. Three methoxy groups lean ca. 5° toward the bismuth center from the ideal sp^2 bond angle, and intramolecular distances [2.993(5)−3.031(6) Å] between the bismuth and oxygen atoms are shorter than the sum of their van der Waals

(8) *N*-Methylacetamide was most likely formed via the Ritter reaction of acetonitrile. Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045.

(9) Benzene was most likely formed via the Bi−C bond cleavage of **1a** by a generated protonic acid.

(10) This compound showed phenyl protons in the ^1H NMR spectrum (in $CDCl_3$) at δ 7.7−7.8 (m, *m*- and *p*-H) and 8.26 (d, J = 7.9 Hz, *o*-H). It also showed a strong ion peak in the FABMS spectrum (in 3-nitrobenzyl alcohol) at 516 that could be assigned to the $[Ph_2BiOCH_2C_6H_4\text{-}3\text{-}NO_2]^+$ ion. These spectral features suggest a Ph_2BiX type of structure.

(11) Parris, G. E.; Long, G. G.; Andrews, B. C.; Parris, R. M. *J. Org. Chem.* **1976**, *41*, 1276.

(12) For example, see: (a) Carty, A. J.; Taylor, N. J.; Coleman, A. W.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1979**, 639. (b) Godfrey, S. M.; McAuliffe, C. A.; Mackie, A. G.; Pritchard, R. G. In *Chemistry of Arsenic, Antimony and Bismuth*; Norman, N. C., Ed.; Blackie Academic and Professional: London, 1998; Chapter 4, pp 159−205.

(13) Recently, aryl- and alkenylboronic acids were found to be potent reagents for preparing aryl- and alkenylbismuthonium salts. (a) Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1998**, *17*, 4332. (b) Matano, Y.; Begum, S. A.; Miyamatsu, T.; Suzuki, H. *Organometallics* **1999**, *18*, 5668.

(14) When the reaction was performed for 48−72 h, the tetraphenylbismuthonium salt was formed in ca. 5−10% yield.

(15) This method was not applicable to the Bi−Bu bond formation; no Bi−C coupling took place between *n*-butylboronic acid and **2a** in the presence of BF_3·OEt_2.

(16) Suzuki, H.; Ikegami, T.; Azuma, N. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1609.

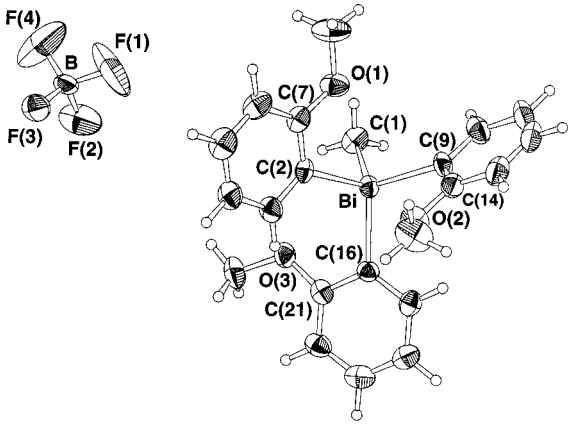


Figure 1. ORTEP diagram for **4d** (30% probability ellipsoids). Selected bond lengths (Å) and angles (deg): Bi−C(1), 2.195(8); Bi−C(2), 2.185(7); Bi−C(9), 2.189(7); Bi−C(16), 2.182(7); C(1)−Bi−C(2), 107.5(3); C(1)−Bi−C(9), 111.6(3); C(1)−Bi−C(16), 113.6(3); C(2)−Bi−C(9), 108.5(3); C(2)−Bi−C(16), 106.1(3); C(9)−Bi−C(16), 109.3(3); O(1)−C(7)−C(2), 115.1(7); O(2)−C(14)−C(9), 114.9(7); O(3)−C(21)−C(16), 114.0(7).

Table 1. Crystal Data for 4d

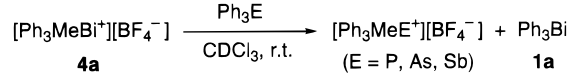
formula	$C_{22}H_{24}BBiF_4O_3$
a (Å)	11.505(1)
b (Å)	12.358(1)
c (Å)	8.696(1)
α (deg)	102.072(8)
β (deg)	100.232(10)
γ (deg)	87.028(8)
V (Å^3)	1189.8(2)
μ(Mo Kα) (cm^{-1})	74.47
space group	$P\bar{1}$
Z value	2
D_{calc} (g cm^{-3})	1.765
no. of reflns collected	5825
no. of unique reflns	5464
R_{int}	0.023
no. of observations ($I > 2.00\sigma(I)$)	3992
no. of variables	281
R	0.036
R_w	0.048
goodness of fit	1.11

radii (ca. 3.8 Å).[17] Thus, the interaction between the cationic bismuth center and the oxygen atoms should be attractive. This type of interaction between the positively charged bismuth(V) and neighboring oxygen atoms was also observed for [(2-$MeOC_6H_4$)$_4$Bi$^+$][Br$^-$][16] and (2-$MeOC_6H_4$)$_3$Bi=NCOCCl$_3$.[18]

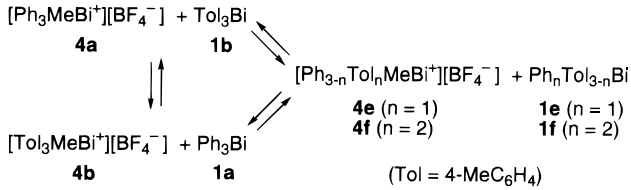
Reactions of Triaryl(methyl)bismuthonium Salts. To investigate the reactivity of triaryl(methyl)bismuthonium salts **4** toward nucleophiles, **4a** was reacted with Ph_3E (E = P, As, Sb), tris(4-methylphenyl)bismuthine, alcohols, water, sodium benzenesulfinate, sodium benzoate, DMF, and thioacetamide.

Treatment of **4a** with triphenylphosphine (1 equiv), triphenylarsine (1 equiv), and triphenylstibine (5 equiv) in $CDCl_3$ at room temperature afforded the methylated phosphonium, arsonium, and stibonium tetrafluoroborates, respectively, together with bismuthine **1a** (Scheme 3). The methyl transfer was complete within a minute in all cases, suggesting that the methylbismuthonium salt **4a** is thermodynamically much less stable than the lighter pnictogen counterparts.

Scheme 3



Scheme 4



Scheme 5

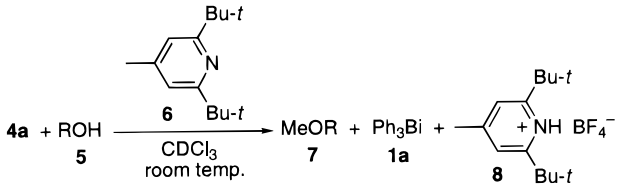


Table 2. Reaction of 4a with Alcohols 5[a]

entry	alcohol (**5**)	ether (**7**)	yield/%[b]
1	MeOH (**5a**)	MeOMe (**7a**)	69
2	EtOH (**5b**)	EtOMe (**7b**)	74
3	*i*-PrOH (**5c**)	*i*-PrOMe (**7c**)	82
4	$PhCH_2OH$ (**5d**)	$PhCH_2OMe$ (**7d**)	95

[a] Reaction was carried out in $CDCl_3$ at room temperature. [b] Yields refer to the NMR yield. Bismuthine **1a** and pyridinium salt **8** were formed quantitatively.

An interesting equilibrium was observed between **4a** and tris(4-methylphenyl)bismuthine (**1b**) (Scheme 4). Treatment of **4a** with an equimolar amount of **1b** in $CDCl_3$ at room temperature slowly afforded **4b** and **1a** at the initial stages of the reaction. After 24 h, however, an equilibrium mixture of four triaryl(methyl)bismuthonium salts **4a**,**b**,**e**,**f** was formed.[19] The mixed type of compounds **4e**,**f** were assigned on the basis of the bismuth-bound methyl peaks in the ^{1}H NMR spectra and by the [$Ph_nTol_{3-n}MeBi^+$] ($n = 0-3$) ion peaks in the FABMS spectra. Reaction between **4b** and **1a** afforded a similar equilibrium mixture after 24 h. In contrast, tetrakis(4-methylphenyl)bismuthonium tetrafluoroborate did not react with **1a** under the same conditions. The observed equilibrium is therefore characteristic of the methylbismuthonium salts **4**, but the reaction course is not clearly understood at present.[20]

Methylbismuthonium salt **4a** reacted with alcohols **5** in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (**6**) to yield alkyl methyl ethers **7** as the exclusive coupling product with good recovery of bismuthine **1a** and pyridinium salt **8** (Scheme 5, Table 2). When treated with methanol (**5a**), ethanol (**5b**), 2-propanol (**5c**), and benzyl alcohol (**5d**), **4a** transferred the methyl group to afford dimethyl ether (**7a**), ethyl methyl ether (**7b**), isopropyl methyl ether (**7c**), and benzyl methyl ether

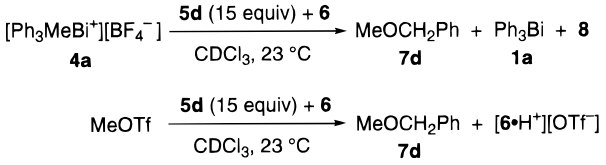
(17) (a) Dean, J. A. *Lange's Handbook of Chemistry*, 11th ed.; McGraw-Hill: New York, 1973; Tables 3−9. (b) Emsley, J. *The Elements*, 3rd ed.; Oxford University Press: Oxford, 1998.

(18) Matano, Y.; Nomura, H.; Shiro, M.; Suzuki, H. *Organometallics* **1999**, *18*, 2580.

(19) A small amount of insoluble substance was also formed.

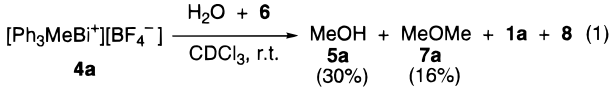
(20) Unidentified trace components in the reaction mixture might cause disproportionation of **1a**,**b** to **1e**,**f**. It is likely that **4a**,**b** transfer the methyl group to these unsymmetrical bismuthines **1e**,**f** to afford **4e**,**f**.

Scheme 6



(**7d**), respectively. Oxidation products such as acetaldehyde (from **5b**), acetone (from **5c**), and benzaldehyde (from **5d**) were not produced at all. The sterically hindered pyridine **6** behaved as a non-nucleophilic base to trap fluoroboric acid. Thus, in the absence of **6**, **4a** reacted with **5** to afford an insoluble substance and benzene in addition to **7**. In this reaction, the Bi−C bonds of **1a** would be cleaved by the generated fluoroboric acid. No reaction took place between alcohols **5** and methyltriphenylphosphonium or methyltriphenylstibonium tetrafluoroborate under the same reaction conditions, suggesting the remarkable nucleofugality of the triphenylbismuthonio group.

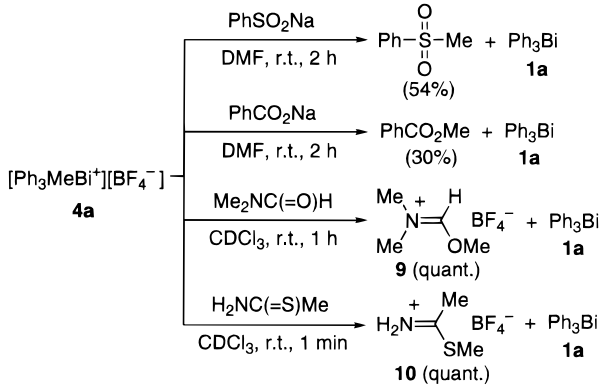
Compound **4a** also reacted with water; treatment of **4a** with an excess of water (5 equiv) in the presence of **6** afforded methanol (**5a**) and dimethyl ether (**7a**) in 30% and 16% yields, respectively (eq 1). In the initial stages of this reaction, **5a** was the sole coupling product. Ether **7a** likely is formed by the reaction of the initially produced **5a** with the remaining bismuthonium salt **4a**.



To compare the leaving ability of the triphenylbismuthonio group with that of triflate, kinetic studies were carried out for the reactions of **5d** with **4a** and methyl triflate (MeOTf) separately (Scheme 6). In the presence of an excess of **5d** (15 equiv), both **4a** and MeOTf were consumed according to first-order kinetics. The pseudo-first-order rate constants (k_{obsd}) observed under the same conditions (in $CDCl_3$ at 23 °C, [**4a**] or [MeOTf] = [**6**] = 0.063 M; [**5d**] = 0.96 M) were 2.9×10^{-4} s^{-1} for **4a** and 1.3×10^{-4} s^{-1} for MeOTf, respectively. The k_{obsd} did not depend on the concentration of the pyridine **6** in the range of 0.063−0.32 M (1−5 equiv), suggesting that **6** is not involved in the rate-determining step of the reaction. These observations indicate that the leaving ability of the triphenylbismuthonio group is about twice as large as that of triflate in the ether formation.

Compound **4a** transferred its methyl group to several *O*- and *S*-nucleophiles with quantitative recovery of bismuthine **1a** (Scheme 7). Reaction of **4a** with sodium benzenesulfinate or sodium benzoate in DMF at room temperature afforded methyl phenyl sulfone or methyl benzoate after aqueous workup. Due to the competing side-reaction with the solvent, the yields of these products were only 30−54%. Actually, **4a** reacted with DMF in $CDCl_3$ at room temperature to afford methoxymethyleneiminium salt **9**[21] quantitatively. This is in contrast to a similar *N*-methylation using methyldiphenylsulfonium tetrafluoroborate, which proceeds only at

Scheme 7



much higher temperatures (100−120 °C).[21] When water was added to the resulting solution, **9** was readily hydrolyzed to yield methyl formate and a dimethylammonium salt.[22] Compound **4a** also reacted with thioacetamide to afford 1-(methylthio)ethyleneiminium salt **10**[23] quantitatively.

In summary, a new method for the synthesis of triaryl(methyl)bismuthonium salts based on the BF_3•OEt_2-promoted reaction of triarylbismuth difluorides with methylboronic acid has been developed. The bismuth center in the tris(2-methoxyphenyl)(methyl)bismuthonium salt possesses a distorted tetrahedral geometry. The methyltriphenylbismuthonium salt has been found to transfer the methyl group to various nucleophiles under mild conditions. The observed reactivity of the methyltriphenylbismuthonium salt differs considerably from that of lighter pnictogen counterparts. This is attributed to the high nucleofugality of the triphenylbismuthonio group.

Experimental Section

General Comments. All reactions with air-sensitive compounds were carried out under an atmosphere of argon. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer (200 MHz for ^1H and 50 MHz for ^{13}C) using $CDCl_3$ as the solvent. Chemical shifts are reported as the relative value vs tetramethylsilane. IR spectra were observed as KBr pellets on a Shimadzu FTIR-8100S spectrophotometer. FABMS spectra were obtained on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University. Dichloromethane (CH_2Cl_2) was distilled from CaH_2 before use. Diethyl ether (Et_2O) was distilled from sodium benzophenone ketyl before use. DMF and CH_3CN were distilled from CaH_2 and stored over 4 Å molecular sieves.

Materials. Triarylbismuth difluorides **2a**−**c** were prepared according to reported procedures.[7b,13b,24] Tris(2-methoxyphenyl)bismuth difluoride (**2d**) was prepared from tris(2-methoxyphenyl)bismuthine and xenon difluoride. Methylboronic acid **3** was purchased from Aldrich. Other reagents were used as commercially received.

Tris(2-methoxyphenyl)bismuth difluoride (2d): mp 215−220 °C (decomp); ^1H NMR δ 3.87 (s, 9H), 7.20−7.30 (m,

(21) Julia, M.; Mestdagh, H. *Tetrahedron* **1983**, *39*, 433.

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6H), 7.46−7.56 (m, 3H), 8.02 (dd, 3H, J = 1.7, 7.7 Hz); FABMS m/z 549 (M^+ − F), 423, 316, 209. Anal. Calcd for $C_{21}H_{21}BiF_2O_3$: C, 44.38; H, 3.72. Found: C, 44.17; H, 3.78.

Reaction of Triphenylbismuthine (1a) with Trimethyloxonium Tetrafluoroborate. To a CH_2Cl_2/CH_3CN solution (1 mL:1 mL) of **1a** (44 mg, 0.10 mmol) was added $[Me_3O^+][BF_4^-]$ (15 mg, 0.10 mmol) at 0 °C, and the resulting mixture was stirred at room temperature. As the reaction proceeded, white insoluble substances were gradually deposited. After 12−14 h, the latter were filtered through Celite and the filtrate was evaporated under reduced pressure to leave an oily residue (21 mg), in which unreacted bismuthine **1a**, a bismuth compound of the type Ph_2BiX, benzene, and *N*-methylacetamide were observed by ^{1}H NMR spectroscopy. The yields of **1a** and the amide were about 20% and 80%, respectively. A similar result was obtained when methyl iodide and silver tetrafluoroborate were used instead of $[Me_3O^+][BF_4^-]$. Under the same conditions, triphenylphosphine, triphenylarsine, and triphenylstibine smoothly reacted with $[Me_3O^+][BF_4^-]$ to give the corresponding onium salts.

Reaction of 1a with Methyl Triflate. To a $CDCl_3$ solution (0.50 mL) of **1a** (10 mg, 0.023 mmol) was added methyl triflate (11 μL, 1.0 mmol) at room temperature, and the resulting solution was monitored by ^{1}H NMR spectroscopy. No bismuth-derived compound except for **1a** was detected after 1 week at room temperature.

Synthesis of Triaryl(methyl)bismuthonium Tetrafluoroborates 4. General Procedure. To a stirred mixture of triarylbismuth difluoride **2** (3.0 mmol), methylboronic acid **3** (2−3 equiv), and CH_2Cl_2 (40 mL) was added $BF_3{\cdot}OEt_2$ (0.46 mL, 3.5 mmol) at −20 °C. The mixture was stirred vigorously for 12−14 h, during which time the temperature was gradually warmed to room temperature. An aqueous solution (10 mL) of $NaBF_4$ (2.2 g, 20 mmol) was then added, and the resulting two-phase solution was vigorously stirred for 30 s. The organic phase was immediately separated, dried over $MgSO_4$, and evaporated under reduced pressure to leave an oily residue. Fractional recrystallization of the residue from Et_2O/CH_2Cl_2 (2:1) twice afforded triaryl(methyl)bismuthonium tetrafluoroborate **4** as a colorless solid. **Methyltriphenylbismuthonium tetrafluoroborate (4a):** mp 137−139 °C; ^{1}H NMR δ 3.29 (s, 3H), 7.50−7.85 (m, 15H); ^{13}C NMR δ 17.36, 131.82, 132.00, 135.67, 136.21; IR ν_{max} 3050, 1568, 1474, 1429, 1325, 1298, 1200−950 (BF_4^-), 729, 695, 534, 523, 446 cm^{-1}; FABMS m/z 455 (M^+ − BF_4), 363, 286, 209. Anal. Calcd for $C_{19}H_{18}BBiF_4$: C, 42.09; H, 3.35. Found: C, 42.02; H, 3.22.

Methyltris(4-methylphenyl)bismuthonium tetrafluoroborate (4b): pasty solid; ^{1}H NMR δ 2.42 (s, 9H), 3.23 (s, 3H), 7.41 (d, 6H, J = 8.0 Hz), 7.59 (d, 6H, J = 8.0 Hz); IR ν_{max} 1576, 1561, 1487, 1450, 1437, 1391, 1306, 1279, 1240, 1177, 1150−900 (BF_4^-), 830, 816, 785, 579, 534, 519, 469 cm^{-1}; FABMS m/z 497 (M^+ − BF_4), 391, 300, 209. Due to the low crystallinity of **4b**, a trace amount of the tetrakis(4-methylphenyl)bismuthonium salt could not be removed completely.

Tris(4-methoxyphenyl)(methyl)bismuthonium tetrafluoroborate (4c): mp 156−159 °C (decomp); ^{1}H NMR δ 3.17 (s, 3H), 3.84 (s, 9H), 7.10 (d, 6H, J = 8.8 Hz), 7.63 (d, 6H, J = 8.8 Hz); IR ν_{max} 1585, 1487, 1440, 1389, 1307, 1296, 1210, 1200−950 (BF_4^-), 791, 560, 532, 521, 480, 473, 430 cm^{-1}; FABMS m/z 545 (M^+ − BF_4), 423, 316, 209. Anal. Calcd for $C_{22}H_{24}BBiF_4O_3$: C, 41.80; H, 3.83. Found: C, 42.03; H, 3.80.

Tris(2-methoxyphenyl)(methyl)bismuthonium tetrafluoroborate (4d): ^{1}H NMR δ 3.29 (s, 3H), 3.87 (s, 9H), 7.18 (dt, 3H, J = 1.1, 7.4 Hz), 7.21 (d, 3H, J = 8.4 Hz), 7.43 (d, 3H, J = 7.6 Hz), 7.61 (m, 3H); IR ν_{max} 1570, 1460, 1428, 1298, 1269, 1231, 1175, 1157, 1150−900 (BF_4^-), 785, 752, 565, 534, 521, 475, 436 cm^{-1}; FABMS m/z 545 (M^+ − BF_4), 423, 316, 209. Anal. Calcd for $C_{22}H_{24}BBiF_4O_3$: C, 41.80; H, 3.83. Found: C, 41.59; H, 3.67. Compound **4d** did not show a definite melting point.

Reaction of 4a with Ph_3E (E = P, As, Sb). To a mixture of **4a** (11.4 mg, 0.021 mmol) and triphenylphosphine (5.8 mg, 0.022 mmol) was added $CDCl_3$ (0.50 mL) in an NMR tube at room temperature, and the resulting colorless solution was measured by ^{1}H NMR. The reaction was complete within a minute, and triphenylbismuthine (**1a**) and methyltriphenylphosphonium tetrafluoroborate were formed quantitatively. Triphenylarsine (6.8 mg, 0.022 mmol) and triphenylstibine (35 mg, 0.10 mmol) also reacted with **4a** (11.4 mg, 0.021 mmol) within a minute in $CDCl_3$ (0.50 mL) to afford the corresponding arsonium and stibonium salts, respectively. These onium salts were characterized by comparison with an authentic specimen.

Methyltriphenylphosphonium tetrafluoroborate:[25] ^{1}H NMR δ 2.88 (d, 3H, J_{HP} = 13.3 Hz), 7.55−7.85 (m, 15H); IR ν_{max} 1200−1000 (BF_4^-) cm^{-1}; FABMS m/z 277 (M^+ − BF_4).

Methyltriphenylarsonium tetrafluoroborate:[26] ^{1}H NMR δ 2.84 (s, 3H), 7.60−7.85 (m, 15H); IR ν_{max} 1200−1000 (BF_4^-) cm^{-1}; FABMS m/z 321 (M^+ − BF_4).

Methyltriphenylstibonium tetrafluoroborate:[26] ^{1}H NMR δ 2.55 (s, 3H), 7.50−7.75 (m, 15H); FABMS m/z 369 (M^+ − BF_4; ^{123}Sb), 367 (M^+ − BF_4; ^{121}Sb).

Reaction of 4a,b with Triarylbismuthines 1b,a. A mixture of **4a** (10.6 mg, 0.020 mmol), **1b** (9.4 mg, 0.020 mmol), and $CDCl_3$ (0.50 mL) was allowed to stand in a sealed NMR tube at room temperature, and the reaction course was monitored by ^{1}H NMR spectroscopy at several intervals. After 24 h, an equilibrium mixture consisting of four triaryl(methyl)bismuthonium salts **4a**,**b**,**e**,**f** (ca. 1:2:3:4) was formed with a small amount of insoluble substance. Treatment of **4b** (11.5 mg, 0.020 mmol) with **1a** (8.6 mg, 0.020 mmol) in $CDCl_3$ (0.50 mL) gave a similar equilibrium mixture after 24 h. Compounds **4e**,**f** were assigned only by ^{1}H NMR and FABMS spectroscopy and have not been isolated. In the ^{1}H NMR spectra of the equilibrium mixtures, the bismuth-bound methyl peaks of **4a**, **4e**, **4f**, and **4b** were observed at δ 3.25, 3.23, 3.21, and 3.19, respectively. In the FABMS spectra, the $[Ph_n(4\text{-}MeC_6H_4)_{3-n}MeBi^+]$ ion peaks derived from **4a**, **4e**, **4f**, and **4b** were observed at 455 (n = 3), 469 (n = 2), 483 (n = 1), and 497 (n = 0). No reaction took place between tetrakis(4-methylphenyl)bismuthonium tetrafluoroborate and **1a** in $CDCl_3$ at room temperature.

Tetrakis(4-methylphenyl)bismuthonium tetrafluoroborate: mp 205−206 °C; ^{1}H NMR δ 2.44 (s, 12H), 7.48 (d, 8H, J = 8.1 Hz), 7.64 (d, 8H, J = 8.1 Hz); IR ν_{max} 1487, 1447, 1391, 1312, 1280, 1210, 1188, 1150−950 (BF_4^-), 799, 519, 475 cm^{-1}; FABMS m/z 573 (M^+ − BF_4), 391, 300, 209. Anal. Calcd for $C_{28}H_{28}BBiF_4$: C, 50.93; H, 4.27. Found: C, 51.00; H, 4.24. This compound was synthesized from $BF_3{\cdot}OEt_2$, **1b**, and 4-methylphenylboronic acid according to the reported procedure.[13]

Reaction of 4a with Alcohols. General Procedure. Alcohol **5** (0.15 mmol) was added to a mixture of **4a** (11.4 mg, 0.021 mmol), 2,6-di-*tert*-butyl-4-methylpyridine **6** (4.6 mg, 0.022 mmol), and $CDCl_3$ (0.50 mL) in an NMR tube, and the resulting clear solution was monitored by ^{1}H NMR spectroscopy at 23 °C. The reaction was complete after 4−7 h. Bismuthine **1a** and pyridinium salt **8** were formed quantitatively. Ethers **7** were identified by NMR spectroscopy.

Dimethyl ether (7a): ^{1}H NMR δ 3.32 (s, 6H).

Ethyl methyl ether (7b):[27] ^{1}H NMR δ 1.17 (t, 3H, J = 7.0 Hz), 3.33 (s, 3H), 3.43 (q, 2H, J = 7.0 Hz).

Isopropyl methyl ether (7c):[27] ^{1}H NMR δ 1.16 (d, 6H, J = 6.0 Hz), 3.31 (s, 3H), 3.48 (sept, 1H, J = 6.0 Hz).

Benzyl methyl ether (7d):[28] ^{1}H NMR δ 3.38 (s, 3H), 4.45 (s, 2H), 7.25−7.42 (m, 5H).

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2,6-Di-*tert*-butyl-4-methylpyridinium tetrafluoroborate (8): ^{1}H NMR δ 1.55 (s, 18H), 2.65 (s, 3H), 7.5 (s, 2H), 11.5 (s, 1H, NH).

Reaction of 4a with Water. Water (2.0 μL, 0.11 mmol) was added to a mixture of **4a** (11.4 mg, 0.021 mmol), **6** (4.6 mg, 0.022 mmol), and $CDCl_3$ (0.50 mL) in an NMR tube, and the resulting solution was allowed to stand at room temperature. After 33 h, methanol (**5a**) and dimethyl ether (**7a**) were formed in 30% and 16% yield, respectively. Bismuthine **1a** and pyridinium salt **8** were formed quantitatively.

Kinetic Measurement on the Reaction of 5d with 4a and MeOTf. Compound **4a** (17.0 mg, 0.0314 mmol), **5d** (50 μL, 0.483 mmol; 15 equiv), **6** (6.5 mg, 0.032 mmol), and $CDCl_3$ (0.50 mL) were mixed well in an NMR tube. The reaction was monitored at 23 °C by ^{1}H NMR spectroscopy using the methyl peaks of **4a** and **7d** as probes. The reaction followed pseudo-first-order kinetics for up to 3−4 half-lives, and the pseudo-first-order rate constant (k_{obsd}) was estimated to be 2.9×10^{-4} s^{-1} ($r^2 = 0.998$). The reaction rate did not depend on the concentration of **6** in the range of 0.063−0.32 M. Similar pseudo-first-order kinetics were observed for the reaction of MeOTf (3.6 μL, 0.032 mmol) with **5d** (15 equiv) in the presence of **6** (1 equiv) under the same conditions, and the k_{obsd} was estimated to be 1.3×10^{-4} s^{-1} ($r^2 = 0.996$).

Reaction of 4a with Sodium Benzenesulfinate. A mixture of **4a** (28 mg, 0.052 mmol), sodium benzenesulfinate dihydrate (52 mg, 0.26 mmol), and DMF (1 mL) was stirred at room temperature for 2 h. Water (3 mL) and Et_2O (3 mL) were added, and the resulting two-phase solution was stirred vigorously. The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 mL × 2). The combined organic extracts were washed with water (2 mL), dried over $MgSO_4$, and evaporated to leave a mixture of bismuthine **1a** (20.8 mg, 91%) and methyl phenyl sulfone (4.4 mg, 54%).

Reaction of 4a with Sodium Benzoate. A mixture of **4a** (33 mg, 0.061 mmol), sodium benzoate (83 mg, 0.58 mmol), and DMF (2 mL) was stirred at room temperature for 2 h. Water (3 mL) and Et_2O (3 mL) were added, and the resulting two-phase solution was stirred vigorously. The organic phase was separated, and the aqueous phase was extracted with Et_2O (3 mL × 2). The combined organic extracts were washed with water (2 mL), dried over $MgSO_4$, and evaporated to leave a mixture of bismuthine **1a** (26 mg, 97%) and methyl benzoate (2.5 mg, 30%).

Reaction of 4a with DMF. A mixture of **4a** (15.1 mg, 0.0279 mmol), DMF (10 μL, 0.26 mmol), and $CDCl_3$ (0.50 mL) was allowed to stand in an NMR tube at room temperature. The reaction was complete within 1 h, and compound **9** and bismuthine **1a** were formed quantitatively.

1-Methoxy-*N*,*N*-dimethylmethyleneiminium tetrafluoroborate (9):[21] ^{1}H NMR δ 3.22 (d, 3H, $J = 1.1$ Hz), 3.44 (d, 3H, $J = 0.8$ Hz), 4.43 (s, 3H), 8.56 (br s, 1H). When water (5 μL) was added to the resulting solution, **9** was immediately converted to dimethylammonium salt and methyl formate.

Reaction of 4a with Thioacetamide. To a $CDCl_3$ solution (0.50 mL) of **4a** (14.5 mg, 0.0268 mmol) was added thioacetamide (2.9 mg, 0.039 mmol), and the resulting mixture was shaken quickly at room temperature. The reaction was complete within a minute, and compound **10** and bismuthine **1a** were formed quantitatively.

1-(Methylthio)ethyleneiminium tetrafluoroborate (10):[23] ^{1}H NMR δ 2.66 (s, 3H), 2.72 (s, 3H), 9.8 (br-s, 2H).

X-ray Crystallographic Analysis of Compound 4d. A colorless crystal of dimensions 0.20 × 0.20 × 0.08 mm, grown from CH_2Cl_2/Et_2O (1:1) at 4 °C, was used for X-ray crystallographic analysis. Data were recorded at 27 °C on a Rigaku AFC7S diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation, using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.0°. Scans of $(1.05 + 0.30 \tan \theta)°$ were made at a speed of 8.0° min^{-1}. The intensities of three representative reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 14.1%. A linear correction factor was applied to the data to account for this phenomenon. An empirical absorption correction based on azimuthal scans of several reflections was applied, which resulted in transmission factors ranging from 0.62 to 1.00. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied. The structure was solved by the Patterson methods[29] and expanded using the Fourier techniques.[30] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[31] Anomalous dispersion effects were included in F_{calc};[32] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[33] The values for the mass attenuation coefficients are those of Creagh and Hubbel.[34] All calculations were performed using the teXsan[35] crystallographic software package of Molecular Structure Corporation. Further details of the crystal structure are provided as Supporting Information.

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Supporting Information Available: Detailed X-ray crystallographic data for **4d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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