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Notes

A New Convenient Synthesis of Triarylbismuthanes Bearing Three Different Aryl Groups by the Grignard Arylation of Unsymmetrical Diarylbismuth Triflate−Hexamethylphosphoric Triamide (HMPA) Complexes

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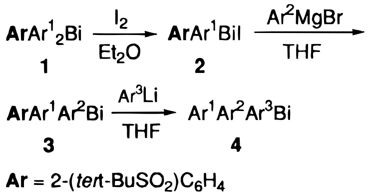
*Summary: Triarylbismuthanes bearing three different aryl groups, $Ar^1Ar^2Ar^3Bi$ (**4**), have been conveniently synthesized by the action of aryl Grignard reagent Ar^3-MgBr on unsymmetrical diarylbismuth triflate−HMPA complexes $Ar^1Ar^2BiOTf(HMPA)_2$ (**8**), which are readily accessible by the selective cleavage of triarylbismuthanes $Ar^1{}_2Ar^2Bi$ (**7**; Ar^1 is more fugacious than Ar^2) with trimethylsilyl triflate in the presence of HMPA.*

Introduction

Although many examples have been reported of chiral organophosphorus(III), organoarsenic(III), and organoantimony(III) compounds, the literature to date contains very few descriptions of chiral organobismuth(III) compounds.[1,2] This would mainly be due to the lack of reliable approaches to such compounds because of their greater instability as compared with those derived from other pnicogen elements.

In 1983, Bras *et al.* first prepared tertiary bismuthanes having three different organyl substituents by the reaction of ArAr′BiBr with an appropriate aryl Grignard reagent, but their isolated yields were low to moderate (10−55%).[1a] We have recently reported a general methodology for the synthesis of chiral triarylbismuthanes **4** based on intramolecular coordination by a sulfonyl group.[1b] In this method, the 2-(*tert*-butylsulfonyl)phenyl group (=**Ar**) plays an important role, in which this auxiliary aryl group not only assures the selective iododearylation of triarylbismuthane (**1**) to diarylbismuth iodide (**2**) but leaves preferentially from bismuthane **3** in the final ligand exchange step, leading to the required chiral triarylbismuthane **4** (Scheme 1).

Scheme 1



In the present work, this selective dearylation−rearylation methodology for the synthesis of chiral triarylbismuthanes has been further elaborated into the use of diarylbismuth triflate−HMPA (HMPA = hexamethylphosphoric triamide) complexes **6** and **8** as the key intermediate (Scheme 2). These triflates are readily accessible in a high state of purity by the cleavage of the respective triarylbismuthanes **5** and **7** with trimethylsilyl triflate in the presence of HMPA. They are stable enough to be handled in open air, are soluble in most common organic solvents, and can be stored without change in a refrigerator.

Results and Discussion

Synthesis of Diarylbismuth Triflate−HMPA Complexes 6. Bismuth compounds of the type Ar_2BiX have usually been prepared by the redistribution reaction between Ar_3Bi and BiX_3, where X denotes a halogen atom other than fluorine.[3] Although quite easy to effect, this methodology has an intrinsic disadvantage; it is based on the equilibration among four different bismuth compounds Ar_nBiX_{3-n} ($n = 0-3$) in a given solution; thus, it is often difficult to obtain the required Ar_2BiX in high yield and in a high state of purity.[4]

An alternative approach to this type of compound involves the selective cleavage of triarylbismuthanes with an appropriate acid reagent. Although somewhat limited in scope, this methodology can provide the required Ar_2BiX in a 100% pure form. As an acid reagent, trimethylsilyl triflate (Me_3SiOTf) proved to be

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(1) ArAr′Ar″Bi type of compounds: (a) Bras, P.; Van Der Gen, A.; Wolters, J. *J. Organomet. Chem.* **1983**, *256*, C1. (b) Suzuki, H.; Murafuji, T. *J. Chem. Soc., Chem. Commun.* **1992**, 1143.

(2) ArAr′BiX (X = halogen or oxygen) type of compounds: (a) Bras, P.; Herwijer, H.; Wolters, J. *J. Organomet. Chem.* **1981**, *212*, C7. (b) Yamamoto, Y.; Chen, X.; Kojima, S.; Ohdoi, S.; Kitano, M.; Doi, Y.; Akiba, K.-y. *J. Am. Chem. Soc.* **1995**, *117*, 3922. (c) Chen, X.; Ohdoi, K.; Yamamoto, Y.; Akiba, K.-y. *Organometallics* **1993**, *12*, 1857. (d) Yamamoto, Y.; Chen, X.; Akiba, K.-y. *J. Am. Chem. Soc.* **1992**, *114*, 7906. (e) Chen, X.; Yamamoto, Y.; Akiba, K.-y.; Yoshida, S.; Yasui, M.; Iwasaki, F. *Tetrahedron Lett.* **1992**, *33*, 6653. (f) Murafuji, T.; Mutoh, T.; Satoh, K.; Tsunenari, K.; Azuma, N.; Suzuki, H. *Organometallics* **1995**, *14*, 3848. (g) Murafuji, T.; Azuma, N.; Suzuki, H. *Organometallics* **1995**, *14*, 1542. (h) Suzuki, H.; Murafuji, T.; Matano, Y.; Azuma, Y. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1169.

(3) For a review, see: Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982**, *82*, 15.

(4) For example, stirring a 2:1 mixture of tris(4-methylphenyl)-bismuthane and $BiCl_3$ in diethyl ether for 5 h at room temperature gave the corresponding diarylbismuth chloride, arylbismuth dichloride, and unreacted bismuthane in the ratio 74:7:19.

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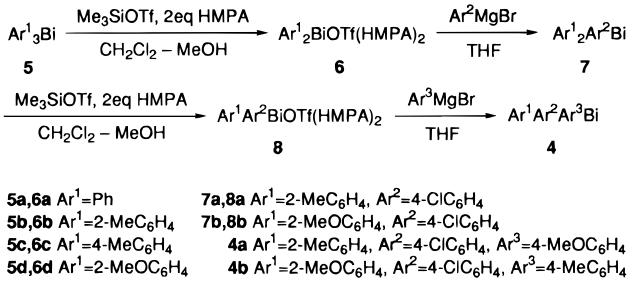
Scheme 2



the most satisfactory for our purpose. Thus, the reaction of Ar^1_3Bi (**5**) with Me_3SiOTf in the presence of two equiv of HMPA in CH_2Cl_2/MeOH at room temperature led to the quantitative formation of $Ar^1_2BiOTf(HMPA)_2$ **6** within a few hours (Scheme 2). In this reaction, triflic acid, generated *in situ* from Me_3SiOTf and MeOH, cleaves the C−Bi bond of **5** to give **6**.

The complexes **6** are stable colorless crystals or oils, readily soluble in CH_2Cl_2, $CHCl_3$, benzene, THF, and MeOH without decomposition. When left in air, some of these complexes slowly absorbed moisture to form the monohydrate $Ar^1_2BiOTf(HMPA)_2(H_2O)$. A similar reaction carried out in the absence of HMPA afforded the Ar^1_2BiOTf−MeOH complexes, which were less stable in open air as compared to **6**. The HMPA ligand is apparently more effective in protecting the triflates from hydrolysis by atmospheric moisture.

The compounds **6** exhibited some characteristic spectral features; ^1H NMR spectra showed a signal due to the *ortho* protons of the aromatic rings at appreciably lower field (δ 8.17−8.37) as compared to those of **5** (δ 7.6−7.8). The methyl protons of HMPA in **6** were observed at slightly higher field (δ 2.42−2.53) than those of free HMPA (δ 2.63). In the IR spectra, broad intense bands due to the triflate group appeared in the range 1350−1100 cm^{-1}. FAB mass spectra displayed a strong peak due to the M^+−OTf and/or M^+−(OTf, HMPA) fragments in support of the cationic nature of the bismuth center. Norman *et al.* have earlier reported the synthesis of a similar type of complex $Ph_2BiBF_4(HMPA)_2$ and elucidated its X-ray structure, in which the central bismuth atom was found to possess a pseudo trigonal bipyramidal structure.[5] On the basis of the spectral features as well as structural analogy, the geometry around the bismuth center of **6** may be taken to be pseudo trigonal bipyramidal, with two aryl groups and a pair of electrons at the equatorial positions and two HMPA ligands at both axial positions. Then, the complex **6** would provide another example of a cationic trivalent bismuth compound with a slightly nucleophilic counteranion.

Synthesis of Mixed Triarylbismuthanes 7. Mixed triarylbismuthanes of the type $Ar^1_2Ar^2Bi$ (**7**) have been prepared by a reaction between Ar^1_2BiX and Ar^2M or between Ar^1_2BiM and Ar^2X, where X is a halogen and M is Li, Na, K, or MgBr.[3] In the present study, we used the former methodology to construct the bismuthane unit $Ar^1_2Ar^2Bi$ (**7**). Treatment of **6** with an excess of Ar^2MgBr in THF at 0 °C readily gave **7** in good yield (Scheme 2). Although the reaction was accompanied to some extent by concurrent disproportionation of bismuthanes, the analytically pure product was easily obtained by recrystallization from MeOH. The previously unknown bismuthanes $Ar^1_2Ar^2Bi$ (**7**) were characterized by NMR, MS, and IR.

Synthesis of Unsymmetrical Diarylbismuth Triflate−HMPA Complexes 8. Mixed triarylbismuthanes **7** were easily transformed into unsymmetrical diarylbismuth triflates **8**, as shown in Scheme 2. The more electron-rich aryl group was preferentially removed from **7**, in accord with the general pattern of the nucleophilic exchange of aromatic ligands. The spectral features of **8** are almost the same as those of **6**, suggesting that compound **8** also possesses the pseudo trigonal bipyramidal structure at the bismuth center. The triflates **8** are stable in the solid state, but they undergo slow redistribution in solution.

Synthesis of Unsymmetrical Triarylbismuthanes 4. Unsymmetrical diarylbismuth triflate−HMPA complexes **8** were treated with an excess of an appropriate aryl Grignard reagent in THF at 0 °C in a manner similar to that used for the synthesis of mixed triarylbismuthanes **7**. Disproportionation of bismuthanes during the Grignard arylation was insignificant, and the required bismuthanes **4** were easily isolated in pure form by recrystallization from MeOH.

Attempts to convert these bismuthanes into bismuthonium compounds bearing four different aryl groups attached to the bismuth atom and resolve the latter into the respective optical antipodes for the first time are now under way.

In conclusion, triarylbismuthanes **4** having three different aryl groups were conveniently prepared by the action of an appropriate aryl Grignard reagent on the unsymmetrical diarylbismuth triflate−HMPA complexes. This new approach circumvents the use of diarylbismuth halides, which are moisture-sensitive and often difficult to obtain in a high state of purity.

Experimental Section

General Comments. All reactions were carried out under an argon atmosphere. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF) were distilled under argon from CaH_2 and sodium benzophenone ketyl, respectively, before use. Other reagents were used as commercially received. All melting points were determined on a Yanagimoto hot-stage apparatus and are uncorrected. ^1H NMR was recorded on a Varian Gemini-200 (200 MHz) or JEOL JNM α 500 (500 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. Coupling constants are given in Hz. IR spectra were observed on a Shimadzu FTIR-8100S spectrophotometer. EIMS spectra at 70 eV were obtained on a Shimadzu GCMS-QP2000A spectrometer and FABMS spectra on a JEOL JMS-HS110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Elemental analyses were performed at the Microanalytical Laboratory of Kyoto University.

Preparation of Diarylbismuth Triflate−HMPA Complexes 6. General Procedure. To a stirred solution of the bismuthane **5** (10 mmol) in HMPA (3.5 mL, 20 mmol)/CH_2Cl_2 (50 mL)/MeOH (5 mL) was added Me_3SiOTf (1.9 mL, 10 mmol) at 0 °C, and the resulting mixture was stirred for 0.5−2 h at room temperature to complete the reaction. The solvent was

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(5) (a) Carmalt, C. J.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Organomet. Chem.* **1993**, *460*, C22. (b) Carmalt, C. J.; Cowley, A. W.; Decken, A.; Norman, N. C. *J. Organomet. Chem.* **1995**, *496*, 59. (c) Clegg, W.; Elsegood, M. R. J.; Errington, R. J.; Fisher, G. A.; Norman, N. C. *J. Mater. Chem.* **1994**, 891. (d) Clegg, W.; Errington, R. J.; Fisher, G. A.; Flynn, R. J.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1993**, 637. (e) Clegg, W.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Chem. Soc., Dalton Trans.* **1992**, 1967.

removed under reduced pressure to give pure **6** as an oily residue or a crystalline solid in quantitative yield.

Diphenylbismuth triflate−HMPA complex (6a): yield 100%. ^{1}H NMR δ 2.52 (d, 36H, J = 9.7 Hz), 7.38 (t, 2H, J = 7.4 Hz), 7.70 (t, 4H, J = 7.6 Hz), 8.29 (d, 4H, J = 7.9 Hz); FABMS (m/z) 721 ($M^+ - OTf$), 542, 465, 388, 363, 286, 209, 180, 179, 135; IR (KBr) 2900, 1500−1430, 1330−1290, 1260−1050, 1032, 990, 752, 733, 696, 639 cm^{-1}. Anal. Calcd for $C_{25}H_{46}BiF_3N_6O_5P_2S$: C, 34.49; H, 5.33; N, 9.65. Found: C, 34.00; H; 5.17; N, 9.48.

Bis(2-methylphenyl)bismuth triflate−HMPA complex (6b): yield 100%. ^{1}H NMR δ 2.42 (d, 36H, J = 9.7 Hz), 2.65 (s, 6H), 7.36 (dt, 2H, J = 1.4, 7.4 Hz), 7.44−7.64 (m, 4H), 8.32 (dd, 2H, J = 1.4, 7.4 Hz); FABMS (m/z) 570 ($M^+ - OTf$, HMPA), 479, 391, 388, 300, 209, 180, 179, 135; IR (KBr) 1464, 1300−1250, 1200−1150, 1034, 981, 750, 638 cm^{-1}. Anal. Calcd for $C_{27}H_{50}BiF_3N_6O_5P_2S$: C, 36.08; H, 5.61; N, 9.35. Found: C, 35.82; H, 5.52; N, 9.26.

Bis(4-methylphenyl)bismuth triflate−HMPA complex (6c): yield 100%. ^{1}H NMR δ 2.33 (s, 6H), 2.53 (d, 36H, J = 9.7 Hz), 7.49 (d, 4H, J = 7.8 Hz), 8.17 (d, 4H, J = 7.8 Hz); FABMS (m/z) 749 ($M^+ - OTf$), 570, 479, 391, 388, 300, 209, 180, 179, 135; IR (KBr) 1487, 1458, 1330−1290, 1260−1050, 1032, 990, 797, 752, 639 cm^{-1}. Anal. Calcd for $C_{27}H_{50}BiF_3N_6O_5P_2S + H_2O$: C, 35.38; H, 5.71; N, 8.99. Found: C, 35.16; H, 5.47; N, 9.31.

Bis(2-methoxyphenyl)bismuth triflate−HMPA complex (6d): yield 100%. mp 93−100 °C dec; ^{1}H NMR δ 2.42 (d, 36H, J = 9.8 Hz), 3.89 (s, 6H), 7.22−7.46 (m, 6H), 8.37 (dd, 2H, J = 1.7, 7.2 Hz); FABMS (m/z) 602 ($M^+ - OTf$, HMPA), 495, 423, 388, 316, 209, 180, 179, 135; IR (KBr) 1570, 1466, 1428, 1350−1260, 1250−1100, 1034, 982, 752, 640 cm^{-1}. Anal. Calcd for $C_{27}H_{50}BiF_3N_6O_7P_2S + H_2O$: C, 34.18; H, 5.52; N, 8.85. Found: C, 33.76; H, 5.18; N, 9.22.

Preparation of Mixed Triarylbismuthanes 7. General Procedure. To a stirred solution of **6** (10 mmol) in THF (50 mL) was added at 0 °C a solution of an appropriate Ar^2MgBr compound (prepared from Ar^2Br (15−25 mmol) and Mg (15−25 mmol)) in THF (60 mL), and the resulting mixture was stirred at the same temperature for 1−2 h to complete the reaction. The mixture was poured into ice-cold saturated aqueous NH_4Cl (30 mL), and the insoluble materials were filtered off through a Celite bed. The organic phase was extracted with benzene (10 mL × 5), and the combined extracts were washed with brine (10 mL × 5), dried (Na_2SO_4), and concentrated under reduced pressure to leave an oily residue, which was crystallized from benzene/MeOH (1/5) to afford **7** as colorless crystals.

(4-Chlorophenyl)bis(2-methylphenyl)bismuthane (7a): yield 85%; mp 88−91 °C (lit.[1a] 80−83 °C). ^{1}H NMR δ 2.41 (s, 6H), 7.11 (dt, 2H, J = 1.4, 7.1 Hz), 7.23−7.40 (m, 6H), 7.54−7.60 (m, 4H); EIMS (m/z) 322, 320, 300, 209; IR (KBr) 1557, 1470, 1455, 1375, 1088, 1046, 1007, 806, 745, 713 cm^{-1}. Anal. Calcd for $C_{20}H_{18}BiCl$: C, 47.77; H, 3.61. Found: C, 47.86; H, 3.56.

(4-Chlorophenyl)bis(2-methoxyphenyl)bismuthane (7b): yield 86%; mp 93−95 °C. ^{1}H NMR δ 3.76 (s, 6H), 6.92 (dt, 2H, J = 1.0, 7.2 Hz), 7.02 (d, 2H, J = 7.2 Hz), 7.23−7.40 (m, 4H), 7.49 (dd, 2H, J = 1.7, 7.2 Hz), 7.56 (d, 2H, J = 8.3 Hz); EIMS (m/z) 322, 320, 316, 209; IR (KBr) 1568, 1460, 1426, 1269, 1230, 1177, 1161, 1115, 1090, 1051, 1020, 1005, 810, 785, 756, 714 cm^{-1}. Anal. Calcd for $C_{20}H_{18}BiClO_2$: C, 44.92; H, 3.39. Found: C, 45.32; H, 3.34.

Preparation of Unsymmetrical Diarylbismuth Triflate−HMPA Complexes 8. Compounds **8a,b** were prepared from **7a,b** according to the same procedure used for the preparation of **6**.

(4-Chlorophenyl)(2-methylphenyl)bismuth triflate−HMPA complex (8a): yield 100%. ^{1}H NMR δ 2.52 (d, 36H, J = 9.6 Hz), 2.67 (s, 3H), 7.33 (dt, 1H, J = 1.6, 7.4 Hz), 7.43 (dt, 1H, J = 1.5, 7.6 Hz), 7.60 (dd, 1H, J = 1.6, 7.6 Hz), 7.65 (d, 2H, J = 8.3 Hz), 8.20 (d, 2H, J = 8.3 Hz), 8.35 (dd, 1H, J = 1.5, 7.4 Hz); FABMS (m/z) 771 ($M^+ - OTf$, ^{37}Cl), 769 ($M^+ - OTf$, ^{35}Cl), 592, 590, 501, 499, 479, 413, 411, 388, 209, 179; IR (neat) 1470, 1294, 1267, 1192, 1163, 1090, 1036, 990, 810, 752, 714 cm^{-1}. Anal. Calcd for $C_{26}H_{47}BiClF_3N_6O_5P_2S + H_2O$: C, 33.32; H, 5.26; N, 8.96. Found: C, 33.18; H, 5.16; N, 9.26.

(4-Chlorophenyl)(2-methoxyphenyl)bismuth triflate−HMPA complex (8b): yield 100%. ^{1}H NMR δ 2.53 (d, 36H, J = 9.6 Hz), 3.93 (s, 3H), 7.16 (m, 1H), 7.25−7.41 (m, 2H), 7.65 (d, 2H, J = 8.4 Hz), 8.16 (d, 2H, J = 8.4 Hz), 8.32 (d, 1H, J = 7.3 Hz); FABMS (m/z) 787 ($M^+ - OTf$, ^{37}Cl), 785 ($M^+ - OTf$, ^{35}Cl), 608, 606, 501, 499, 495, 429, 427, 388, 209, 179; IR (neat) 1572, 1462, 1431, 1296, 1269, 1192, 1163, 1094, 1034, 988, 810, 752, 714 cm^{-1}. Anal. Calcd for $C_{26}H_{47}BiClF_3N_6O_6P_2S$: C, 33.39; H, 5.06; N, 8.98. Found: C, 33.62; H, 5.07; N, 8.95.

Preparation of Unsymmetrical Triarylbismuthanes 4. Compounds **4a,b** were prepared by the reaction of **8a,b** with (4-methoxyphenyl)- and (4-methylphenyl)magnesium bromides, respectively, according to the same procedure used for the preparation of **7**.

(4-Chlorophenyl)(4-methoxyphenyl)(2-methylphenyl)bismuthane (4a): yield 80%; mp 120−123 °C. ^{1}H NMR δ 2.39 (s, 3H), 3.79 (s, 3H), 6.92 (d, 2H, J = 8.6 Hz), 7.13 (dt, 1H, J = 1.7, 8.4 Hz), 7.22−7.38 (m, 4H), 7.53−7.65 (m, 5H); EIMS (m/z) 322, 320, 316, 300, 209; IR (KBr) 1578, 1487, 1374, 1279, 1242, 1181, 1084, 1057, 1024, 1003, 810, 745, 710 cm^{-1}. Anal. Calcd for $C_{20}H_{18}BiClO$: C, 46.30; H, 3.50. Found: C, 46.47; H, 3.46.

(4-Chlorophenyl)(2-methoxyphenyl)(4-methylphenyl)bismuthane (4b): yield 70%; mp 99−102 °C. ^{1}H NMR δ 2.32 (s, 3H), 3.77 (s, 3H), 6.94 (dt, 1H, J = 7.3, 0.9 Hz), 7.02 (d, 1H, J = 7.7 Hz), 7.19 (d, 2H, J = 7.3 Hz), 7.28 (d, 2H, J = 8.3 Hz), 7.35 (t, 1H, J = 9.1 Hz), 7.55 (d, 1H, J = 7.4 Hz), 7.56 (d, 2H, J = 8.2 Hz), 7.60 (dt, 2H, J = 1.7, 8.3 Hz); EIMS (m/z) 429, 427, 407, 322, 320, 316, 300, 209; IR (KBr) 1570, 1458, 1428, 1370, 1300, 1220, 1170, 1085, 1050, 1025, 1005, 795, 756, 710 cm^{-1}. Anal. Calcd for $C_{20}H_{18}BiClO$: C, 46.30; H, 3.50. Found: C, 46.41; H, 3.50.

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