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Effect of π-accepting substituent on the reactivity and spectroscopic characteristics of triarylbismuthanes and triarylbismuth dihalides

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Abstract

Competitive chlorination of *p*-substituted triarylbismuthanes **1** [$(p\text{-XC}_6\text{H}_4)_3\text{Bi}$; **a**: X = OMe, **c**: Cl, **d**: CO_2Et, **e**: CF_3, **f**: CN, **g**: NO_2] and trimesitylbismuthane $(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_3\text{Bi}$ **1h** by sulfuryl chloride was carried out against **1b** (X = H) and the effect of these substituents on the formation of triarylbismuth dichlorides **2** was studied. The relative ratios **2**/**2b** decreased with increasing electron-withdrawing ability of the substituents (**2a**/**2b** = 53/47, **2c**/**2b** = 33/67, **2d**/**2b** = 35/65, **2e**/**2b** = 29/71, **2f**/**2b** = 16/84, **2g**/**2b** = 0/100, **2h**/**2b** = 46/54), indicating a lowering of reactivity of the lone pair on the bismuth atom. Pd-Catalyzed degradation of **2a**–**g** and their difluorides **3** giving biaryls **4** was promoted by the electron-withdrawing *p*-substituents in the equatorial aryl groups but suppressed by the more electronegative fluorine atoms in the apical positions. This is in fairly good accord with the stability of the trigonal bipyramidal geometry. The ^{13}C NMR study of **1**–**3** showed that the signals due to the ipso carbons (C1) attached to the bismuth atom shift downfield with increasing electron-withdrawing nature of the *p*-substituents. No such tendency was observed in other aromatic ring carbons. The electronic effect on the C1 atoms, similar to that on the chlorination of **1** and degradation of **2** and **3**, indicates the significant participation of the C1 atoms in these reactions through the Bi–C1 bonds.

Keywords: Bismuth; Electron-withdrawing group; Oxidative chlorination; Biaryl formation; *ipso*-Carbon; ^{13}C NMR study

1. Introduction

Organobismuth compounds have been receiving increasing interest owing to their versatile reactivity and properties [1]. Triarylbismuth dihalides (Ar_3BiX_2; X = F, Cl) are utilized as stable and useful precursors of various organobismuth(V) derivatives. From the viewpoint of organic transformation, triarylbismuth dichlorides are efficient arylating reagents of phenols and carbonyl compounds [2]. Despite such availability, however, the number of this class of derivatives is not so large since the aryl groups introducible into the bismuth center have been limited. In particular, few reports on the derivatives bearing π-accepting substituents have appeared in the literature [3] due to lack of general synthetic methods for the parent triarylbismuthanes. It is an important issue for us to know how electronic effect affects the reactivity and properties of organobismuth compounds. In order to address this issue, we have recently established a convenient method for the synthesis of triarylbismuthanes **1d**, **1f** and **1g** bearing a π-accepting ester, cyano and nitro group in the *p*-position of each aromatic ring, respectively [4], the synthesis of which has

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been difficult by conventional methods. This paper describes the electronic effect of *p*-substituents on the oxidative chlorination of **1** to form triarylbismuth dichlorides **2**, Pd-catalyzed biaryl formation of **2** and difluorides **3** and spectroscopic characteristics of **1**–**3**. Systematic studies from the viewpoint of the electronic effect have been restricted in organobismuth chemistry [3b,5], although the structural aspects from the steric viewpoint based on kinetic stabilization have so far been discussed extensively [6].

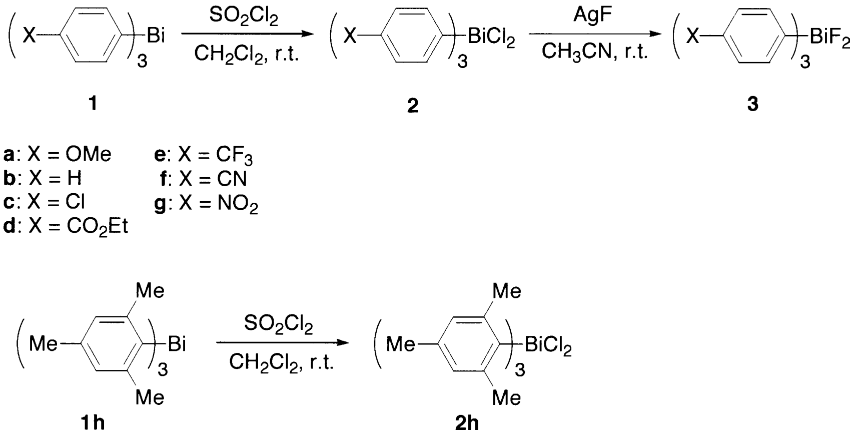
2. Results and discussion

2.1. Oxidative chlorination of triarylbismuthanes *1* with sulfuryl chloride

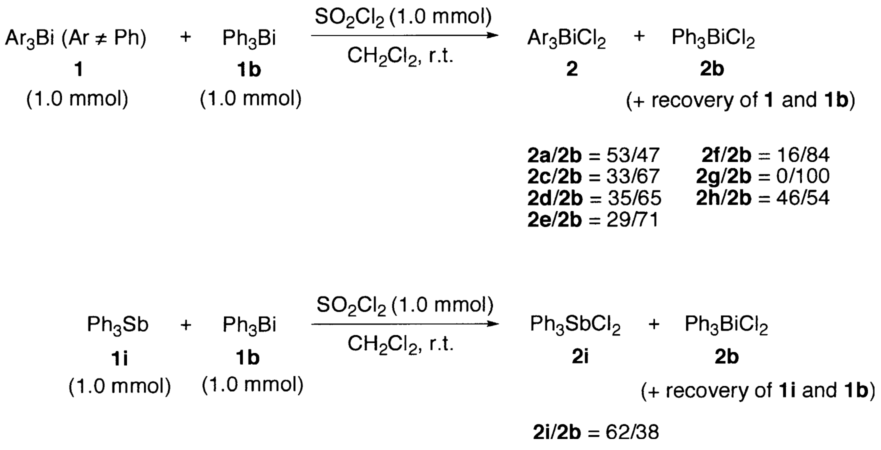
While the chlorination of **1a**–**e** and **1h** completed quickly, that of **1f** and **1g** required a longer reaction time (1–2 h) for completion (Scheme 1). Competitive chlorination of **1** carried out against **1b** revealed that the relative ratios **2**/**2b** (estimated by ^{1}H NMR) decrease with increasing electron-withdrawing nature of the *p*-substituent (Scheme 2). In the competitive chlorination of **1g**, **2g** did not form at all. As shown in Fig. 1, a good linear relationship with a negative slope was obtained between these ratios and the Hammett σ_p constants [7] ($n = 6$, $r = 0.90$). The bulky mesityl groups minimally affected the chlorination of **1h** (**2h**/**2b** = 46/54). Such electronic effect should be stressed since the lone pair of the bismuth atom is inherently an s-character and cannot efficiently overlap with the 2p orbitals of the aromatic ring carbons, although the lone pair on the phosphorus atom of triarylphosphines is delocalized into the aromatic rings by the electron-accepting *p*-substituents [8]. The lowered reactivity of **1** by the electron-accepting *p*-substituents is consistent with the generation of chloronium cation, which is proposed in the chlorination of sulfides at the sulfur atom [9]. The competitive chlorination of triphenylstibine **1i** (**2i**/**2b** = 62/38) reflects the lower s-character of the lone pair on the antimony atom.

2.2. Synthesis of triarylbismuth difluorides *3* and their characterization by ^{19}F NMR spectrum

Recently, it has been found that triarylbismuth difluorides are versatile precursor for the synthesis of bismuthonium salts [10–12]. Development of these methods enables exploration of new research fields of organobismuth(V) derivatives which have been inaccessible by conventional methods. The number of difluorides has been, however, extremely limited compared to triarylbismuthanes and triarylbismuth dichlorides. Thus, a series of difluorides **3a**–**g** were synthesized from dichlorides **2a**–**g** by the chlorine–fluorine exchange with use of AgF (Scheme 1) and studied by ^{19}F NMR spectrum. Few derivatives have been characterized by ^{19}F NMR spectrum [13]. The exchange reaction proceeded smoothly irrespective of the nature of the *p*-substituents. The signals due to the fluorine atoms of **3** appeared around δ_F −160.0 as a sharp singlet and their chemical shifts did not show the dependence of the *p*-substituents (Table 1). The similarity of the δ_F values in **3** indicates that the geometry of the bismuth center in triarylbismuth dihalides is not affected by the electronic effect of the *p*-substituents and governed by the apicophilicity of the halogen atoms, thus adopting a trigonal bipyramidal structure like **2b** [14b] and **3b** [14a]. Recently, several examples of reversed apicophilicity have been found in the trigonal bipyramidal phosphorus systems [15]. Such structural characteristics of triarylbismuth dihalides is in contrast to those of the related organobismuth(V) derivative pentaarylbismuth [5c,16], in which the geometry of the bismuth center changes from the square pyramidal to the trigonal bipyramidal depending on the electronic effect of the aryl groups.



Scheme 1.



Scheme 2.

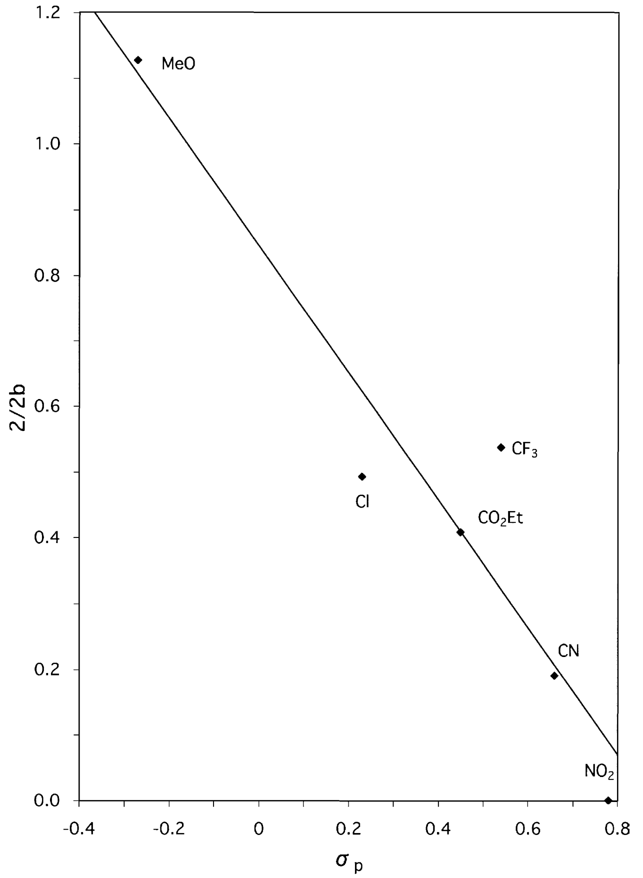


Fig. 1. Hammett plot.

Table 1
^{19}F NMR spectral data (δ) and coupling constants (J_{CF}) of **3** in $CDCl_3$

	δ_F	δ_C, $^2J_{CF}$	δ_C, $^3J_{CF}$
3a	−158.45 (s)	–[a]	–[a]
3b[b]	−161.26 (s)	153.55 (t, 9.2)	134.31 (t, 3.1)
3c	−160.08 (s)	150.83 (t, 10.0)	135.24 (t, 3.1)
3d	−160.37 (s)	157.65 (t, 9.2)	134.13 (t, 3.8)
3e	−161.92 (s), −64.44 (s, CF_3)	156.22 (t, 8.4)	134.76 (t, 3.8)
3f	−162.16 (s)	157.12 (t, 10.0)	134.98 (t, 3.8)
3g	−158.68 (s)	158.41 (t, 10.0)	135.29 (t, 3.8)

[a] Not observed.

[b] In [13a], the δ_F value of **3b** is reported to be −161.3.

2.3. Biaryl formation by Pd-catalyzed coupling reaction of 2 and 3

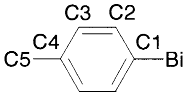
It is known that **2b** undergoes Pd-catalyzed degradation to form **4b** quantitatively [17]. All the three phenyl groups are coupled as the product. In the presence of $Pd(OAc)_2$ catalyst, the coupling reaction of *p*-substituted **2** produced the corresponding biaryls **4** quickly in 85–90% yields (Eq. 1). The similar reaction using $Pd(PPh_3)_4$ catalyst, however, proceeded sluggishly, depending on the *p*-substituents. In order to compare the effect of the substituents, the coupling reaction was carried out independently for **2a**, **2b**, **2e**, **2f** and their difluorides **3** in $CDCl_3$ at 40 °C for 1 h and the recovery (%) of the respective dihalides was estimated by ^{1}H NMR spectrum. The results are as follows: **2a** (96), **2b** (82), **2e** (39), **2f** (27), **3a** (96), **3b** (82), **3e** (74) and **3f** (67%). With increasing electron-withdrawing nature of the substituents, the reactivity increased and such tendency was more remarkable in **2**. These findings are fairly in good accord with the stability of the trigonal bipyramidal structure based on the apicophilicity [18].

$$\underset{\textbf{2a–g}}{Ar_3BiCl_2} \xrightarrow[\text{THF, r.t.}]{Pd(OAc)_2,\ Et_3N} \underset{\textbf{4a–g}}{Ar\text{–}Ar} \qquad (1)$$

2.4. Characterization of 1–3 by ^{13}C NMR spectrum

The aromatic ring carbons of **1**–**3** were all assigned and their chemical shifts (δ_C) are summarized in Table 2, along with those of the parent *mono*-substituted benzenes **5** [19]. The signals due to the *ipso*-carbons (C1) attached to the bismuth atom appeared largely downfield

Table 2
^{13}C NMR spectral data (δ) of **1**–**3** in $CDCl_3$



		C1	C2	C3	C4	C5	CH_2	CH_3
	a	145.06	138.71	116.27	159.26			55.01
	b	155.09	137.53	130.47	127.73			
	c	152.70	138.53	130.67	134.13			
1	**d**	161.66	137.42	131.03	130.18	166.62	61.43	14.60
	e[a]	159.85	137.75	127.32	130.51	124.11		
	f	162.20	137.95	133.95	111.42	118.52		
	g	164.40	138.34	125.48	148.24			
	a	146.73	135.90	116.72	161.72			55.60
	b	155.63	134.17	131.43	131.19			
	c	153.18	135.55	131.66	138.49			
2	**d**	159.82	134.25	132.54	133.58	165.21	61.69	14.23
	e[a]	158.31	134.87	128.65	134.04	123.15		
	f	159.16	135.05	135.05	116.27	116.99		
	g	160.32	135.41	126.41	149.94			
	a	144.36	135.38	116.55	162.15			55.49
	b	153.55	134.31	131.85	131.43			
	c	150.83	135.24	131.45	138.84			
3	**d**	157.65	134.13	132.15	133.96	165.35	61.65	14.24
	e[a]	156.22	134.76	128.26	134.47	123.15		
	f	157.12	134.98	134.74	116.68	117.02		
	g	158.41	135.29	126.02	150.50			
	a	120.7	129.5	114.1	159.9			
	b	128.5	128.5	128.5	128.5			
	c	126.5	129.5	128.7	134.9			
5[b]	**d**	132.4	128.0	129.5	131.0			
	e	131.8	128.8	125.3	131.0			
	f	132.8	129.2	132.1	112.8			
	g	134.7	129.8	124.2	149.1			

[a] Quartet, J_{CF}=around 3.6, 33.0 and 271.3 Hz for C3, C4 and C5, respectively.

[b] **5a**–**d**, **5f** and **5g**: [19a]. **5e**: [19b].

compared to those of the parent **5** (about 25–30, 27 and 25 ppm in **1**, **2** and **3**, respectively). A similar tendency was found with respect to the C2 atoms, but the differences were not so large as observed in the C1 atoms (about 9 ppm in **1** and about 6 ppm in **2** and **3**). The coupling constants $^2J_{CF}$ and $^3J_{CF}$ in **3** were around 9.5 and 3.5 Hz, respectively, and did not show the clear dependence of the *p*-substituent (Table 1). The chemical shifts of the C3 and C4 atoms were close to those of the corresponding carbon atoms of **5**. With respect to the C4 atoms, in particular, little difference was observed between **1** and **5**. These findings suggest that the effect of the bismuth atom is inductively transmitted to the aromatic ring carbons.

An outstanding feature is in the chemical shifts of the ipso C1 atoms, which shifted downfield with increasing electron-withdrawing nature of the *p*-substituents. No such tendency was observed in other aromatic carbons. It is established that the chemical shifts of the C1 atom of **5** are correlated with the Hammett σ_p constants and total charge density on the carbon atom [20]. Linear relationships were shown between the σ_p constants ($n = 7$) and the C1 chemical shifts of **1**–**3** as well as those of **5** with the following positive slopes (**1**: 17.0, $r = 0.89$, **2**: 11.7, $r = 0.81$, **3**: 12.1, $r = 0.83$, **5**: 12.0, $r = 0.88$). The electronic effect on the C1 atoms, which is similar to that on the chlorination of **1** and degradation of **2** and **3**, indicates the significant participation of the C1 atoms in these reactions through the Bi–C1 bonds.

A series of pentacoordinate trifluorosilicates bearing various *p*-substituents in the aromatic ring have been characterized by ^{13}C NMR spectrum in comparison with the parent tetracoordinate silanes [21]. This study suggests that π-polarization takes place in the aromatic rings of the silicates with change in the geometry from the tetracoordinate to the pentacoordinate silicon center. Table 3 shows the differences in chemical shift between **1** and **2** ($\Delta_2 = \delta_2 - \delta_1$) and between **1** and **3** ($\Delta_3 = \delta_3 - \delta_1$) when the geometry of the bismuth center changes from the pyramid of **1** to the trigonal bipyramid

Table 3
The difference in the chemical shifts between **1** and **2** (Δ_2) and between **1** and **3** (Δ_3)s

	Δ_2				Δ_3			
	C1	C2	C3	C4	C1	C2	C3	C4
a	1.67	−2.81	0.45	2.46	−0.70	−3.33	0.28	2.89
b	0.54	−3.36	0.96	3.46	−1.54	−3.22	1.38	3.70
c	0.48	−2.98	0.99	4.36	−1.87	−3.29	0.78	4.71
d	−1.84	−3.17	1.51	3.40	−4.01	−3.29	1.12	3.78
e	−1.54	−2.88	1.33	3.53	−3.63	−2.99	0.94	3.96
f	−3.04	−2.90	1.10	4.85	−5.08	−2.97	0.79	5.26
g	−4.08	−2.93	0.93	1.70	−5.99	−3.05	0.54	2.26

of **2** and **3**. The values Δ_2(C1) and Δ_3(C1) increased negatively with increasing electron-withdrawing nature of the *p*-substituents and the latter was negatively larger than the former. The Δ_2(C2) and Δ_3(C2) values were approximately constant (around −3 ppm) irrespective of the *p*-substituents and apical halogen atoms. With respect to the C3 and C4 atoms, the Δ values were all positive and outstanding regularity was not found. These data show that similar π-polarization arises in the aromatic rings of **2** and **3** with the charge distribution of the C1 and C2 atoms negative and that of the C3 and C4 atoms positive. Furthermore, the influence of the *p*-substituents on the π-polarization is marked in the C1 carbons with increasing electron-accepting nature of the substituents and such tendency is more pronounced in **3** rather than **2**, although the C2, C3 and C4 carbons do not suffer from the outstanding substituent effect in the π-polarization.

3. Experimental

Dichloromethane, acetonitrile and THF were distilled from calcium hydride under nitrogen before use. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a BRUKER AVANCE 400S spectrometer with TMS as an internal standard. ^{19}F NMR spectra were measured in $CDCl_3$ on a BRUKER AVANCE 400S spectrometer with benzotrifluoride (−64.0 ppm) as an internal standard. IR spectra were observed as KBr pellets on a Nicolet Impact 410 spectrophotometer.

3.1. Reaction of *1* with sulfuryl chloride: general procedure

To a solution of triarylbismuthane **1** (1 mmol) in dichloromethane (5 ml) was added at room temperature a 1.0 M solution of sulfuryl chloride in the same solvent (1 ml). After completion of the reaction (checked by TLC), the resulting mixture was concentrated to leave a residue, which was crystallized by an addition of hexane to give the product as colorless crystals.

*Tris(4-methoxyphenyl)bismuth dichloride (**2a**):* Yield 85%; m.p. 128–130 °C (lit. [3b], 135 °C); ^{1}H NMR δ 3.85 (s, 9H), 7.12 (d, 6H, J = 9.1 Hz), 8.42 (d, 6H, J = 9.1 Hz); Anal. Calc. for $C_{21}H_{21}BiO_3Cl_2$: C, 41.97; H, 3.45. Found: C, 41.89; H, 3.52%.

*Triphenylbismuth dichloride (**2b**):* Yield 90%; m.p. 152–154 °C (lit. [22], 156–158 °C; ^{1}H NMR δ 7.54 (t, 3H, J = 7.3 Hz), 7.67 (t, 6H, J = 7.5 Hz), 8.53 (d, 6H, J = 8.2 Hz).

*Tris(4-chlorophenyl)bismuth dichloride (**2c**):* Yield 91%; m.p. 188–190 °C (lit. [23], 170 °C); ^{1}H NMR δ 7.63 (d, 6H, J = 8.7 Hz), 8.47 (d, 6H, J = 8.7 Hz). Anal. Calc. for $C_{18}H_{12}BiCl_5$: C, 34.82; H, 1.96. Found: C, 35.13; H, 1.97%.

*Tris(4-ethoxycarbonylphenyl)bismuth dichloride (**2d**):* Yield 90%; m.p. 142–144 °C (lit. [3c], 138–139 °C); ^{1}H NMR δ 1.40 (t, 9H, J = 7.1 Hz), 4.41 (q, 6H, J = 7.1 Hz), 8.32 (d, 6H, J = 8.6 Hz), 8.61 (d, 6H, J = 8.6 Hz); IR (cm^{-1}): 1723, 1584, 1390, 1271, 1104, 1001, 749. Anal. Calc. for $C_{27}H_{27}BiCl_2O_6$: C, 44.71; H, 3.65. Found: C, 44.53; H, 3.74%.

*Tris(4-trifluoromethylphenyl)bismuth dichloride (**2e**):* Yield 87%; m.p. 137–138 °C) (lit. [5b], 140–143 °C); ^{1}H NMR δ 7.94 (d, 6H, J = 8.4 Hz), 8.71 (d, 6H, J = 8.4 Hz). Anal. Calc. for $C_{21}H_{12}BiF_9Cl_2$: C, 35.44; H, 1.67. Found: C, 35.23; H, 1.69%.

*Tris(4-cyanophenyl)bismuth dichloride (**2f**):* Yield 91%; m.p. 189–191 °C; ^{1}H NMR δ 7.97 (d, 6H, J = 8.6 Hz), 8.72 (d, 6H, J = 8.6 Hz); IR (cm^{-1}): 2238, 1575, 1475, 1388, 992, 825. Anal. Calc. for $C_{21}H_{12}BiCl_2N_3$: C, 43.03; H, 2.06; N, 7.17. Found: C, 43.40; H, 2.26; N, 7.40%.

*Tris(4-nitrophenyl)bismuth dichloride (**2g**):* Yield 88%; m.p. 175–177 °C (lit. [3b], 165 °C); ^{1}H NMR δ 8.53 (d, 6H, J = 9.1 Hz), 8.81 (d, 6H, J = 9.1 Hz); IR (cm^{-1}): 1601, 1559, 1524, 1466, 1389, 1350, 1312, 992, 846, 734. Anal. Calc. for $C_{18}H_{12}BiCl_2N_3O_6$: C, 33.46; H, 1.87; N, 6.50. Found: C, 33.20; H, 2.06; N, 6.24%.

*Tris(2,4,6-trimethylphenyl)bismuth dichloride (**2h**):* Yield 90%; m.p. 155–160 °C (decomp.) (lit. [23], 150 °C, decomp.); ^{1}H NMR δ 2.32 (s, 9H), 2.72 (s, 18H), 7.15 (s, 6H); ^{13}C NMR δ 21.24, 25.80, 132.59, 141.57, 142.29, 167.97.

*Triphenylantimony dichloride (**2i**):* Yield 92%; m.p. 139–141 °C (lit. [24], 139–142 °C); ^{1}H NMR δ 7.56 (m, 9H), 8.24 (m, 6H); ^{13}C NMR δ 129.59, 131.74, 134.11, 139.92.

3.2. Synthesis of **3**: general procedure

A mixture of triarylbismuth dichloride **2** (1 mmol) and silver fluoride (2.4 mmol) was stirred in acetonitrile (5 ml) at room temperature for 1 h. The precipitated insoluble substances were filtered off and the filtrate was concentrated to leave an oily residue, which was crystallized by an addition of hexane to give the product.

*Tris(4-methoxyphenyl)bismuth difluoride (**3a**):* Yield 86%; oil (lit. [10], oil); ^{1}H NMR δ 3.82 (s, 9H), 7.13 (d, 6H, $J = 9.0$ Hz), 8.09 (d, 6H, $J = 9.0$ Hz); Coupling constants $^2J_{CF}$ and $^3J_{CF}$ could not be obtained since the coupling of the fluorine atoms with the C1 and C2 atoms were not clearly observed.

*Triphenylbismuth difluoride (**3b**):* Yield 96%; m.p. 158–160 °C (lit. [13a], 158 °C); ^{1}H NMR δ 7.45 (t, 3H, $J = 8.2$ Hz), 7.65 (t, 6H, $J = 7.6$ Hz), 8.22 (d, 6H, $J = 8.2$ Hz).

*Tris(4-chlorophenyl)bismuth difluoride (**3c**):* Yield 90%; m.p. 68–70 °C (lit. [25], 97–103 °C); ^{1}H NMR δ 7.64 (d, 6H, $J = 8.6$ Hz), 8.14 (d, 6H, $J = 8.6$ Hz). Anal. Calc. for $C_{18}H_{12}BiCl_3F_2$: C, 37.46; H, 1.99. Found: C, 37.12; H, 2.08%.

*Tris(4-ethoxycarbonylphenyl)bismuth difluoride (**3d**):* Yield 87%; m.p. 190–192 °C; ^{1}H NMR δ 1.40 (t, 9H, $J = 7.1$ Hz), 4.25 (q, 6H, $J = 7.1$ Hz), 8.30 (d, 6H, $J = 7.2$ Hz), 8.32 (d, 6H, $J = 7.2$ Hz); IR (cm^{-1}): 1725, 1580, 1392, 1271, 1100, 1000, 750. Anal. Calc. for $C_{27}H_{27}BiF_2O_6$: C, 46.93; H, 3.91. Found: C, 46.60; H, 3.91%.

*Tris(4-trifluoromethylphenyl)bismuth difluoride (**3e**):* Yield 85%; m.p. 132–134 °C; ^{1}H NMR δ 7.94 (d, 6H, $J = 8.2$ Hz), 8.40 (d, 6H, $J = 8.2$ Hz). Anal. Calc. for $C_{21}H_{12}BiF_{11}$: C, 36.97; H, 1.77. Found: C, 36.78; H, 1.53%.

*Tris(4-cyanophenyl)bismuth difluoride (**3f**):* Yield 88%; m.p. 188–190 °C; ^{1}H NMR δ 7.97 (d, 6H, $J = 8.5$ Hz), 8.38 (d, 6H, $J = 8.5$ Hz); IR (cm^{-1}): 2233, 1578, 1524, 1474, 1389, 1008, 831. Anal. Calc. for $C_{21}H_{12}BiF_2N_3$: C, 45.58; H, 2.19; N, 7.59. Found: C, 45.79; H, 2.01; N, 7.32%.

*Tris(4-nitrophenyl)bismuth difluoride (**3g**):* Yield 87%; m.p. 205–210 °C (decomp.); ^{1}H NMR δ 8.49 (d, 6H, $J = 9.0$ Hz), 8.54 (d, 6H, $J = 9.0$ Hz); IR (cm^{-1}): 1600, 1564, 1536, 1468, 1391, 1358, 1311, 1004, 848, 734. Anal. Calc. for $C_{18}H_{12}BiF_2N_3O_6$: C, 35.25; H, 1.97; N, 6.85. Found: C, 35.50; H, 2.10; N, 7.05%.

3.3. Biaryl formation by Pd-catalyzed coupling reaction of **2** and **3**: general procedure

Under argon, Pd(0) catalyst was prepared from $Pd(OAc)_2$ (0.05 mmol) and triethylamine (0.1 mmol) in THF (2 ml). Then a solution of triarylbismuth dichloride **2** or difluoride **3** (0.5 mmol) in the same solvent (1 ml) was added to the catalyst and the resulting mixture was stirred at room temperature for 1 h. Filtration of insoluble black substances deposited during the reaction followed by concentration of the filtrate gave biaryl **4** (Yields are based on the formation of 0.75 mmol of **4**).

4a: Yield 85% (0.64 mmol); m.p. 175–176 °C (lit. [26], 176–177 °C; **4b**: Yield 85% (0.64 mmol); m.p. 70 °C (lit. [26], 70–71 °C; **4c**: Yield 90% (0.67 mmol); m.p. 146–147 °C (lit. [27], 147–148 °C); **4d**: Yield 90% (0.67 mmol): m.p. 111–112 °C (lit. [28], 110–112 °C; **4e**: Yield 86% (0.65 mmol); 83–84 °C (lit. [29], 82–87 °C); **4f**: Yield 86% (0.65 mmol); m.p. 232–234 °C (lit. [27], 233–234 °C); **4g**: Yield 86% (0.65 mmol); m.p. 235–237 °C (lit. [30], 228–233 °C).

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References

[1] H. Suzuki, T. Ogawa, N. Komatsu, Y. Matano, T. Murafuji, T. Ikegami, Organobismuth Chemistry, Elsevier, Amsterdam, 2001.

[2] (a) J.-P. Finet, Chem. Rev. 89 (1989) 1487;
(b) T. Arnauld, D.H.R. Barton, J.-F. Normant, E. Doris, J. Org. Chem. 64 (1999) 6915;
(c) A. Fedorov, S. Combes, J.-P. Finet, Tetrahedron 55 (1999) 1341.

[3] (a) M.M. Rahman, Y. Matano, H. Suzuki, Organometallics 16 (1997) 3565;
(b) D.H.R. Barton, N.Y. Bhatnagar, J.-P. Finet, W.B. Motherwell, Tetrahedron 42 (1986) 3111;
(c) A.N. Nesmeyanov, T.P. Tolstaya, L.S. Isaeva, Dokl. Akad. Nauk SSSR 122 (1958) 614.

[4] T. Murafuji, K. Nishio, M. Nagasue, A. Tanabe, M. Aono, Y. Sugihara, Synthesis (2000) 1208.

[5] (a) Y. Yamamoto, X. Chen, S. Kojima, K. Ohdoi, M. Kitano, Y. Doi, K.-y. Akiba, J. Am. Chem. Soc. 117 (1995) 3922;
(b) X. Chen, K. Ohdoi, Y. Yamamoto, K.-y. Akiba, Organometallics 12 (1993) 1857;
(c) K. Seppelt, Adv. Organomet. Chem. 34 (1992) 207.

[6] (a) T. Sasamori, N. Takeda, M. Fujio, M. Kimura, S. Nagase, N. Tokitoh, Angew. Chem., Int. Ed. Engl. 41 (2002) 139;
(b) N. Tokitoh, Y. Arai, R. Okazaki, S. Nagase, Science 277 (1997) 78;
(c) B. Twamley, C.D. Sofield, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 121 (1999) 3357;
(d) Y. Matano, H. Nomura, H. Suzuki, M. Shiro, H. Nakano, J. Am. Chem. Soc. 123 (2001) 10954;
(e) Y. Matano, M. Kinoshita, H. Suzuki, Bull. Chem. Soc. Jpn. 65 (1992) 3504.

[7] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.

[8] W.-N. Chou, M. Pomerantz, J. Org. Chem. 56 (1991) 2762.

[9] (a) D.L. Tuleen, J. Org. Chem. 32 (1967) 4006;
(b) D.L. Tuleen, V.C. Marcum, J. Org. Chem. 32 (1967) 204.

[10] Y. Matano, S.R. Begum, T. Miyamatsu, H. Suzuki, Organometallics 17 (1998) 4332.

[11] Y. Matano, N. Azuma, H. Suzuki, J. Chem. Soc., Perkin Trans. 1 (1994) 1739.

[12] Y. Matano, M.M. Rahman, M. Yoshimune, H. Suzuki, J. Org. Chem. 64 (1999) 6924.

[13] (a) I. Ruppert, V. Bastian, Angew. Chem., Int. Ed. Engl. 17 (1978) 214;
(b) T. Lewe, D. Naumann, G. Nowicki, H. Schneider, W. Tyrra, Z. Anorg. Allg. Chem. 623 (1997) 122;
(c) A. Schmuck, K. Seppelt, Chem. Ber. 122 (1989) 803.

[14] (a) V.V. Sharutin, O.K. Sharutina, I.V. Egorova, T.K. Ivanenko, V.K. Bel'skii, Russ. J. Gen. Chem. 72 (2002) 44;
(b) D.M. Hawley, G. Ferguson, J. Chem. Soc. (A) (1968) 2539.

[15] (a) P. Kommana, N. Satish Kumar, Jagadese J. Vittal, E.G. Jayasree, E.D. Jemmis, K.C. Kumara Swamy, Org. Lett. 6 (2004) 145;
(b) S. Kojima, K. Kajiyama, M. Nakamoto, K.-y. Akiba, J. Am. Chem. Soc. 118 (1996) 12866;
(c) S.-y. Matsukawa, K. Kajiyama, S. Kojima, S.Y. Furuta, Y. Yamamoto, K.-y. Akiba, Angew. Chem., Int. Ed. Engl. 41 (2002) 4718.

[16] (a) A. Schmuck, D. Leopold, S. Wallenhauer, K. Seppelt, Chem. Ber. 123 (1990) 761;
(b) A. Schmuck, J. Buschmann, J. Fuchs, K. Seppelt, Angew. Chem., Int. Ed. Engl. 26 (1987) 1180;
(c) A. Schmuck, P. Pyykko, K. Seppelt, Angew. Chem., Int. Ed. Engl. 29 (1990) 213.

[17] D.H.R. Barton, N. Ozbalik, M. Ramesh, Tetrahedron 44 (1988) 5661.

[18] (a) Organoantimony(V) compounds bearing a trigonal bipyramidal geometry, K.-y. Akiba, T. Okinaka, M. Nakatani, Y. Yamamoto, Tetrahedron Lett. 28 (1987) 3367;
(b) K.-y. Akiba, Pure Appl. Chem. 68 (1996) 837.

[19] (a) E. Breitmaier, W. Voelter, Carbon-13 NMR Spectroscopy, VCH, Weinheim, 1987, Chapter 4;
(b) D.F. Ewing, Org. Magn. Reson. 12 (1979) 499.

[20] (a) G.L. Nelson, G.C. Levy, J.D. Cargioli, J. Am. Chem. Soc. 94 (1972) 3089;
(b) H. Spiesecke, W.G. Schneider, J. Chem. Phys. 35 (1961) 731.

[21] K. Tamao, T. Hayashi, Y. Ito, Organometallics 11 (1992) 182.

[22] H. Suzuki, T. Ikegami, Y. Matano, N. Azuma, J. Chem. Soc., Perkin Trans. 1 (1993) 2411.

[23] L.A. Zhitkova, N.I. Sheverdina, K.A. Kocheshkov, Zh. Obshch. Khim. 8 (1938) 1839.

[24] D.V. Moiseev, A.V. Gushchin, A.S. Shavirin, Y.A. Kursky, V.A. Dodonov, J. Organomet. Chem. 667 (2003) 176.

[25] H. Imazaki, M. Fujikawa, T. Konishi, Y. Kawaguchi, Jpn. Kokai (1988) 174926;
Chem. Abstr. 111 (1989) 154111j.

[26] Y. Tamura, M.-W. Chun, K. Inoue, J. Minamikawa, Synthesis (1978) 822.

[27] A. Jutand, A. Mosleh, J. Org. Chem. 62 (1997) 261.

[28] G.W. Ebert, J.W. Cheasty, S.S. Tehrani, E. Aouad, Organometallics 11 (1992) 1560.

[29] S.D. Ross, I. Kuntz, J. Am. Chem. Soc. 74 (1952) 1297.

[30] D.F. DeTar, A.A. Kazimi, J. Am. Chem. Soc. 77 (1955) 3842.