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Synthesis and structure of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines

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Abstract

Hypervalent organobismuth compounds, 6-*tert*-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines, with 13 different substituents on the bismuth atom including halogens, alkyl, alkenyl, alkynyl, aryl, or phenylthio groups have been synthesized. A key compound, 12-chloro-6-*tert*-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine, which is a precursor for other azabismocines, has been synthesized by two different procedures; one is based on Akiba's method using 2-bromobenzylbromide as one of the starting materials and the other is a newly developed one using a cheaper starting material, 2-chlorobenzyl chloride. The structures of 12 new bismuth compounds were determined by X-ray diffraction. The eight-membered tetrahydroazabismocine ring has proved to be highly flexible and the hypervalent Bi–N bond distances vary ranging from 2.568(3) to 2.896(5) Å, depending on the electronic nature of the substituents on the bismuth atom. The Bi–N bond distances have good linear relationship against Hammett's σ_m constants.

Keywords: Bismuth; Organobismuth compounds; Hypervalent; X-ray diffraction

1. Introduction

Bismuth compounds attract increasing interests as reagents as well as catalysts in organic synthesis [1]. We have recently reported that organobismuth compounds are useful reagents for the cross-coupling reaction with organic halides and triflates [2,3]. In particular, hypervalent organobismuth compounds, 6-*tert*-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines **1**, are highly reactive and recoverable reagents for the cross-coupling reaction with aryl bromides [3a] and aryl and alkenyl chlorides [3b].

5,6,7,12-Tetrahydrodibenz[c,f][1,5]azabismocines were first synthesized by Akiba and co-workers and their basic structural and chemical properties were reported [4]. They were also reported to act as antibacterial agents, fungicides, algaecides, antifouling agents in a patent [5]. Since we required a large amount of and various types of compounds **1**, following synthetic studies have been done; (1) a new synthetic procedure for the construction of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine structure using cheaper starting materials and (2) introduction of various groups on the bismuth atom of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine. In addition, the structures of 12 new bismuth compounds have been determined by X-ray diffraction.

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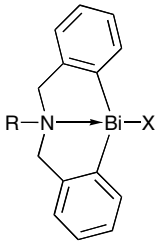


R = *t*Bu

	X		X
1a	F	**1h**	3,4-$(CH_2O_2)C_6H_3$
1b	Cl	**1i**	2,4,6-$(MeO)_3C_6H_2$
1c	Br	**1j**	$CMe{=}CH_2$
1d	I	**1k**	C≡CPh
1e	C_6F_5	**1l**	Me
1f	3,5-$(CF_3)_2C_6H_3$	**1m**	SPh
1g	Ph		

R = Me

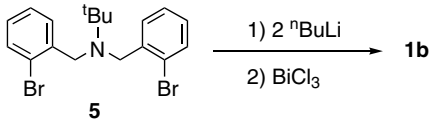
	X		X
2a	F	**2e**	4-$(CF_3)C_6H_4$
2b	Cl	**2f**	4-MeC_6H_4
2c	I	**2g**	Me
2d	Ph		

2. Results and discussion

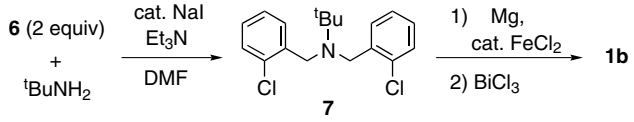
2.1. Syntheses

Akiba and co-workers synthesized the key compound **2b**, which was a precursor for other compounds **2a** and **2c**–**2g**, by the reaction of $BiCl_3$ and (2-$LiC_6H_4CH_2)_2MeN$. The latter compound was in situ generated by the reaction of 2 equiv of ^nBuLi and (2-$BrC_6H_4CH_2)_2MeN$ (**3**), which in turn was prepared from 2-$BrC_6H_4CH_2Br$ (**4**) and $MeNH_2$. A similar procedure is applicable to **1b** by using (2-$BrC_6H_4CH_2)_2{}^tBuN$ **5** (Scheme 1), which was prepared from **4** and $^tBuNH_2$ and used for the synthesis of related silicon compounds by Corriu and co-workers [6]. The reaction of $BiCl_3$ and (2-$LiC_6H_4CH_2)_2{}^tBuN$ in situ generated from **5** afforded **1b** in 65–80% isolated yields (four runs in 29–100 mmol scales were performed). However, it became clear that **1b** obtained by this procedure was contaminated with a small amount (~10%) of bromide **1c**; the latter compound probably arose from the metathesis of **1b** with in situ generated LiBr or derived from $BiCl_nBr_{3-n}$ ($n = 0$–2) formed by the metathesis of $BiCl_3$ and LiBr. The amount of contaminant **1c** in **1b** could be reduced by treatment with aqueous NH_4Cl or HCl solution.

Since one of the starting materials, **4**, is rather expensive compound, we examined to use a much cheaper starting material, 2-$ClC_6H_4CH_2Cl$ **6**, instead of **4**, which also expected to exclude the bromide contamination



Scheme 1. Synthesis of **1b** from **5**.

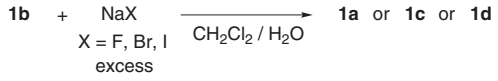


Scheme 2. Synthesis of **1b** starting from **6**.

(Scheme 2). However, required (2-$ClC_6H_4CH_2)_2{}^tBuN$ (**7**) was not obtained efficiently by the procedure for the synthesis of **3**, i.e., reaction of $^tBuNH_2$ with 2 equiv of **6** in dmf at reflux in the presence of K_2CO_3; introduction of the second 2-chlorobenzyl group was slow and the prolonged reaction resulted in the formation of a large amount of by-products. The addition of a catalytic amount of KI [7] improved the reactivity of **6** and gave **7** in 37% yield, while the formation of bis(2-chlorobenzyl)carbonate became competitive to that of **7**. The use of stronger base, NaH, did not afford **7** at all, instead resulted in the formation of *trans*-1,2-bis(2-chlorophenyl)ethene in 54% yield. Finally we found that the use of Et_3N as a base in the presence of a catalytic amount of NaI afforded **7** in 70–84% isolated yields (four runs in 0.04–1.5 mol scales were performed).

Formation of di-Grignard reagent from **7** did not proceed at all by the usual procedure, but was accomplished in a high yield by using a catalytic amount of $FeCl_2$ as reported by Bogdanović and Schwickardi [8]. $Fe(acac)_2$ similarly worked albeit slightly less efficient than $FeCl_2$. Subsequent reaction with $BiCl_3$ afforded **1b** in 41–62% isolated yields (five runs in 0.007–0.23 mol scales were performed). This new procedure using cheaper starting material and reagent is probably applicable not only to bismuth compounds but also to related compounds of silicon [6,9], phosphorous [10], antimony[4a,9], sulfur [11], selenium[12], tellurium[13], and zirconium [14].

Synthesis of other halogen derivatives **1a**, **1c** and **1d** was first examined by the halogen exchange reaction using an excess of NaX (Scheme 3). Conversion of **1b** to **1c** or **1d** was almost quantitative and pure **1c** and **1d** were obtained in more than 90% yields. On the other hand, conversion of **1b** to fluoride **1a** was about 40% even 100 equiv of NaF was used, and isolation of **1a** was not successful. However, treatment of **1b** with 2 equiv of Bu_4NF in thf afforded **1a** nearly quantitatively, although again the isolation of **1a** in pure form was not successful because **1b** easily regenerated during isolation process. The procedure used for the synthesis of fluoride **2a** (KF in dmf) by Akiba was also unsuccessful for the synthesis of **1a** [4a]. Finally we succeeded in isolating



Scheme 3. Halogen exchange reaction of **1b**.

pure **1a** by the reaction of phenyl compound **1g** (vide infra) with an excess of a dilute aqueous HF solution. Iodide **1d** was also obtained by the reaction of **1g** with I_2, which is expected to proceed through pentavalent bismuth intermediate that forms **1d** and PhI [15].

Introduction of organic groups on the bismuth atom of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine was accomplished by the reaction of **1b** with organolithium reagents as reported by Akiba and co-workers [4] or with Grignard reagents (Table 1, entries 1–10). Similarly, PhS group was easily introduced by the reaction of **1b** with PhSLi to give **1m** (Table 1, entry 11). In two cases, i.e., for **1g** and **1l**, both of organolithium and Grignard reagents were tested. In both cases, organolithium reagents afforded the desired products in higher yields than Grignard reagents (Table 1, entries 3–4 and 9–10). When **1h** was synthesized by the reaction of **1b** with commercial 3,4-$(CH_2O_2)C_6H_4MgBr$, once **1h** was produced in a good yield as judged by ^1H NMR analysis. However, the amount of **1h** decreased with the formation of bromide **1c** during prolonged reaction and/or work-up process. This is probably because **1h** reacted with "MgBrX" (X = Cl or Br) generated during the reaction to form **1c**; indeed a separate experiment showed that **1h** reacted with $MgBr_2 \cdot OEt_2$ in thf-d_8 to form bromide **1c** in ca. 30% yield after heating at 50 °C for 3 h, although the resulting magnesium species was not identified. Phenyl compound **1g** is less reactive to $MgBr_2 \cdot OEt_2$ and gave **1c** in 5% yield after heating at 80 °C for 3 h. The reactivity difference between **1h** and **1g** toward $MgBr_2 \cdot OEt_2$ agrees well with the difference in their yields obtained by the reaction of **1b** with Grignard reagents (Table 1, entries 4–5).

An alternative method for the preparation of **1e**–**1l** is the reaction of $RBiX_2$ with $(2\text{-}LiC_6H_4CH_2)_2{}^tBuN$. $RBiX_2$ can be obtained by metathesis of R_3Bi and 2 equiv of BiX_3 [16]. The reaction of $PhBiBr_2$ with $(2\text{-}LiC_6H_4CH_2)_2{}^tBuN$ efficiently proceeded to afford **1g** in 97% yield.

Table 1
Synthesis of **1e**–**1m**

1b + RLi or RMgX or PhSLi → **1e**–**1m**

Entry	RM	Product	Yield[a] (%)
1	C_6F_5Li	**1e**	66
2	3,5-$(CF_3)C_6H_3Li$	**1f**	76
3	PhLi	**1g**	81
4	PhMgBr	**1g**	65
5	3,4-$(CH_2O_2)C_6H_3MgBr$	**1h**	24
6	2,4,6-$(MeO)_3C_6H_2Li$	**1i**	17
7	$CH_2{=}C(Me)MgBr$	**1j**	74
8	$PhC{\equiv}CLi$	**1k**	85
9	MeLi	**1l**	89
10	MeMgBr	**1l**	15
11	PhSLi	**1m**	64

[a] Isolated yield.

Isolation of the products was generally easily performed by recrystallization, Al_2O_3 column chromatography or solvent extraction. However, the isolation of **1i** was rather troublesome because **1i** was not stable to chromatography (silica gel, alumina, florisil) and the separation of a by-product, 1,3,5-trimethoxybenzene, was not easy and impure **1i** did not crystallize easily. Therefore, **1i** was isolated only in a low yield by repeated fractional solvent extraction and fractional precipitation procedure.

Halides **1a**–**1d** are stable to air and can be stored under air. Aryl-, alkenyl-, alkynyl-, and alkyl-substituted compounds **1e**–**1l** in the solid state can be handled under air for hours without noticeable change, but are less stable to air than halides **1a**–**1d** and should be stored under an inert atmosphere.

2.2. Molecular structure

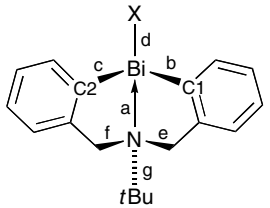
Existence of hypervalent bonds in 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines was confirmed by Akiba and co-workers [4] through the NMR spectroscopy of **2a**–**2g** in solution as well as single crystal X-ray analysis of **2e** and **2f** in the solid state. ^1H and ^{13}C NMR chemical shifts of the methyl group on nitrogen in **2a**–**2d** and **2g** largely affected by the substituents on the bismuth atom (i.e., F, Cl, I, Ph and Me) and showed linear relationship against Hammett's σ_m constants of the substituents [4a]. This result suggests that the transannular bonds are flexible and affected by the substituents on the bismuth atom. Indeed, X-ray analysis of **2e** and **2f** showed that the Bi–N bond distances were influenced by the electronic nature of the substituents [4b].

In order to obtain more detailed information on the structure of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines, we have determined the structures of 12 compounds, **1a**–**1e** and **1g**–**1m**, by single crystal X-ray analysis. Selected bond distances and angles are summarized in Table 2.

Bi–N distances range from 2.568(3) to 2.896(5) Å. As shown in Fig. 1, Bi–N distances have good linear relationship against Hammett's σ_m constants [17] of the substituents on the bismuth atom as observed for the ^1H and ^{13}C NMR chemical shifts by Akiba (from [17], Hammett's σ_m constants are available for 9 compounds among the 12 compounds analyzed by X-ray).

Halides **1a**–**1d** are monomeric in the solid state, although **1a** was obtained as a hydrate and two molecules of **1a** were connected each other through hydrogen bonds between H_2O molecules and F atoms (Fig. 2(a)). Structurally characterized bismuth fluorides are limited and seven examples are found in the Cambridge Structural Database (CSD) [4b,18,19], and one example was recently reported [20]. Among them only one is Bi(III) [19a] and the others are Bi(V) compounds including pentavalent derivatives of **2e** and **2f**. The reported

Table 2
Selected bond distances (Å) and angles (°) for compounds **1a**–**1e** and **1g**–**m**



Bond or angle	**1a**	**1b**	**1c**	**1d**	**1e**	**1g**[a]	**1h**	**1i**	**1j**	**1k**	**1l**	**1m**[a]
a	2.574(4)	2.568(3)	2.559(4)	2.569(3)	2.700(5)	2.836(6)	2.823(6)	2.875(4)	2.826(5)	2.740(2)	2.894(4)	2.669(4)
b	2.246(6)	2.241(3)	2.247(5)	2.254(4)	2.244(6)	2.270(8)	2.277(7)	2.258(4)	2.243(7)	2.252(4)	2.275(7)	2.256(4)
c	2.234(6)	2.250(5)	2.247(5)	2.256(4)	2.265(6)	2.284(8)	2.269(7)	2.263(4)	2.262(7)	2.257(3)	2.266(6)	2.251(4)
d	2.190(4)	2.663(1)	2.7912(5)	3.0139(3)	2.349(6)	2.286(8)	2.306(7)	2.293(4)	2.306(7)	2.289(4)	2.264(6)	2.634(1)
ab	72.6(2)	75.1(1)	75.3(1)	74.7(1)	72.5(2)	70.0(2)	69.2(2)	69.5(1)	70.3(2)	71.7(1)	69.3(2)	72.1(1)
ac	74.9(2)	73.1(1)	72.9(1)	73.0(1)	71.1(2)	69.6(2)	69.5(2)	69.3(1)	68.8(2)	70.1(1)	68.8(2)	72.0(1)
ad	153.6(2)	158.73(9)	159.83(9)	161.06(7)	153.4(2)	153.3(2)	152.4(2)	154.0(1)	151.9(2)	153.6(1)	150.4(2)	155.53(8)
bc	94.6(2)	93.6(1)	93.9(2)	95.6(1)	99.5(2)	97.6(3)	99.0(2)	99.3(1)	99.2(3)	91.2(1)	98.1(2)	97.0(2)
bd	88.7(2)	90.8(1)	91.4(1)	93.36(9)	90.2(2)	93.1(3)	91.9(3)	92.4(1)	90.5(3)	90.9(1)	91.3(2)	93.3(1)
cd	88.6(2)	92.4(1)	93.4(1)	94.02(9)	92.9(2)	93.5(3)	95.0(2)	96.6(2)	95.6(3)	91.2(1)	93.3(2)	91.1(1)
ae	101.6(3)	105.0(2)	105.0(3)	104.7(2)	102.2(3)	100.5(4)	101.3(4)	98.6(2)	101.7(3)	104.3(2)	99.9(3)	102.2(2)
af	104.4(3)	102.3(2)	102.2(3)	101.9(2)	102.1(3)	101.9(4)	100.3(4)	98.2(2)	101.8(4)	100.1(2)	98.9(3)	102.1(2)
ag	115.9(3)	114.2(2)	113.9(3)	115.2(2)	116.0(4)	116.6(5)	116.8(4)	121.6(3)	115.8(4)	114.1(2)	119.9(4)	115.9(3)
others										1.195(5) (C≡C)		101.3(2) (Bi–S–C)

[a] Average values of two independent molecules in the unit cell are shown.

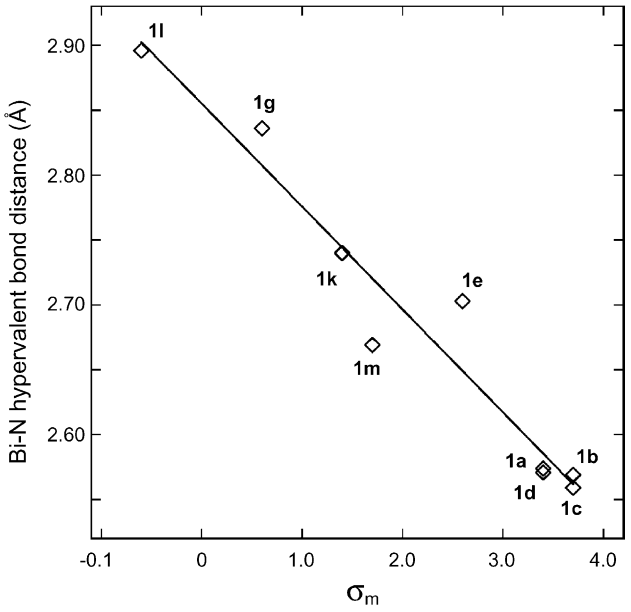


Fig. 1. Relationship between Bi–N hypervalent bond distances and Hammett's σ_m constants.

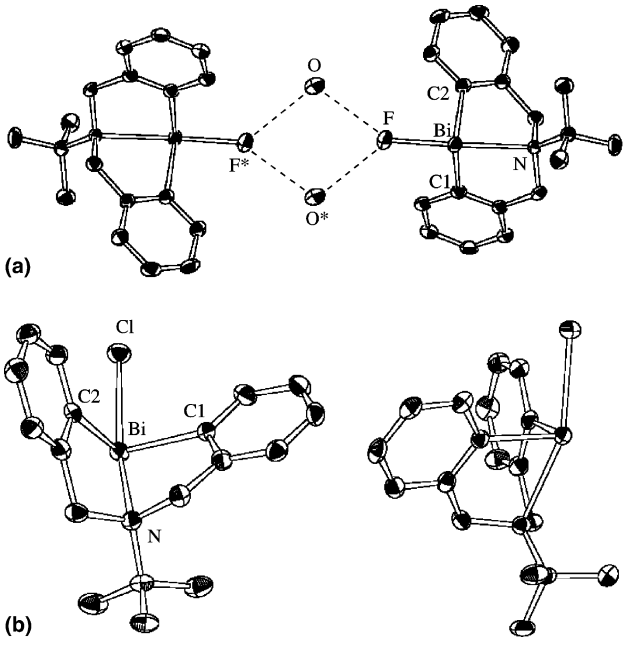
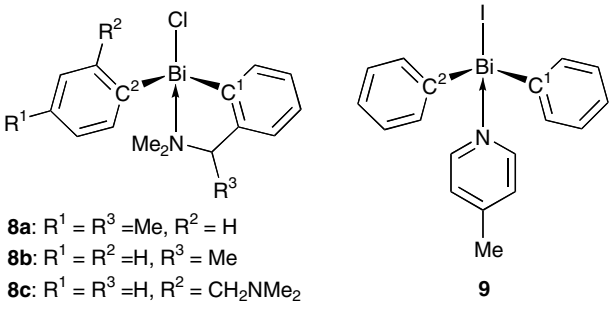


Fig. 2. Molecular structure of (a) **1a** · H_2O and (b) **1b**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity.

Bi–F distances range from 2.088(8) to 2.222(4) Å except those of $(C_{14}H_9)_3BiF_2$ [19c] and Ph_3BiF_2 [19d], which are considerably long (2.498(8) and 2.53(1)–2.59(1) Å, respectively). The Bi–F distance of **1a**, 2.190(4) Å, is within the normal range.

The structure of chloride **1b** (Fig. 2(b)) has good similarity to those of bismuth clorides **8a**–**8c** [21] that have (2-dimethylaminomethyl)phenyl ligands. Although non-chelating N–Bi–C^2 angles (86.5(2)–89.0(2)°) in **8a**–**8c** are much wider than the chelating one (73.1(1)°) in **1b**, other important bond lengths and angles have good similarity (for **8a**–**8c**, Bi–N 2.525(6)–2.570(5) Å and Bi–Cl 2.634(6)–2.700(2) Å, N–Bi–Cl 161.7(4)–165.1(1)°, N–Bi–C^1 72.0(6)–72.7(7)° and C^1–Bi–C^2 93.7(2)–98.0(8)°). Structural similarity is also observed between iodides **1d** and **9**, the latter has a non-chelating 4-methylpyridine ligand [22]. Structural parameters of **1d** and **9** are very similar (for **9**, Bi–N 2.604(7) Å, Bi–I 3.0229(8) Å, C^1–Bi–C^2 96.2(3)°, C^1–Bi–I 90.8(2)°, C^2–Bi–I 94.2(2)°) except for N–Bi–I 174.2(2)°, N–Bi–C1 86.8(2)° and N–Bi–C2 80.8(2)°; the eight-membered ring in **1d** forces the nitrogen atom deviate from the axial position of trigonal bipyramidal geometry. This structural similarity suggests that the eight-membered tetrahydroazabismocine ring are quite flexible and therefore the Bi–N bond distances well reflect the nature of the substituents on the bismuth centers.



Molecular structure of **1e**, **1j**, **1k** and **1l** are shown in Figs. 3–6, respectively. The structural parameters of 12-oraganyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocines **1e**–**1l** are very similar to those of **2e** and **2f** [4b], although C1–Bi–C2 angles of **1e**–**1l** (91.2(1)–99.5(2)°) are smaller than those of **2e** and **2f** (101.7(1)–102.3(2)),

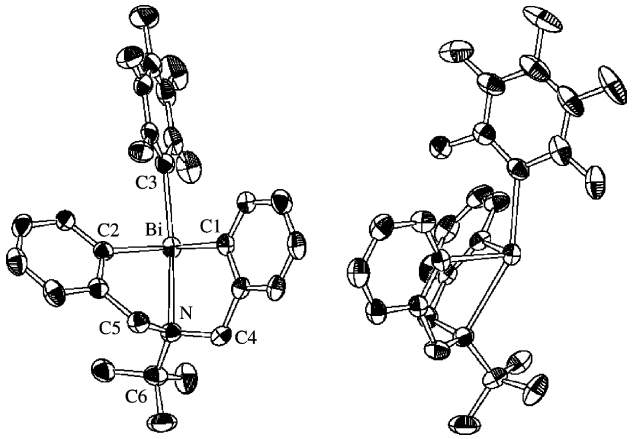


Fig. 3. Molecular structure of **1e**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity.

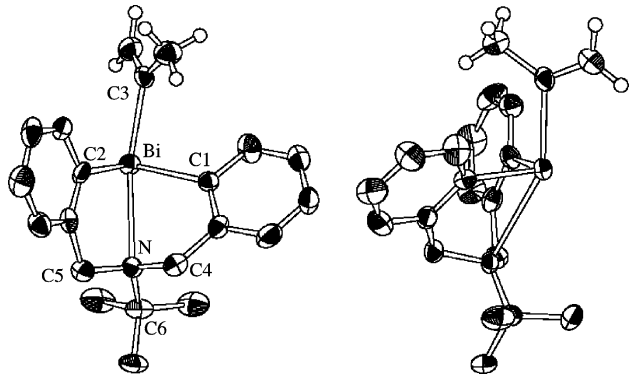


Fig. 4. Molecular structure of **1j**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were shown only for the isopropenyl group for clarity.

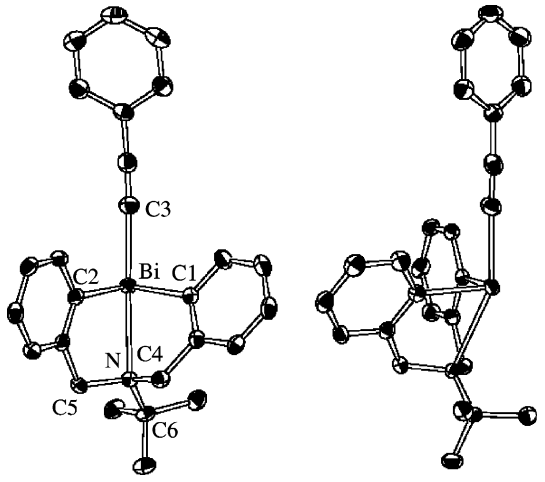


Fig. 5. Molecular structure of **1k**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity.

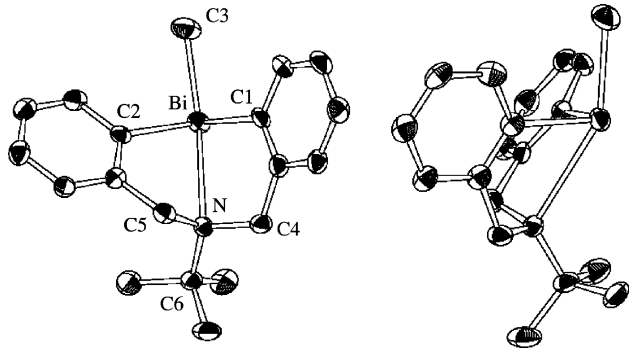


Fig. 6. Molecular structure of **1l**. Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms were omitted for clarity.

which may reflect the difference of the substituents on the nitrogen atom. The exocyclic Bi–C distances in **1e**–**1l** do not simply reflect the difference of electronic properties of C_{sp}, C_{sp^2} and C_{sp^3} atoms. The Bi–C_{sp} distance in **1k** (2.289(4) Å) is longer than those in three alkynyl bismuth compounds found in CSD (2.151(8)–2.249(6) Å) [15,18,23].

3. Conclusions

A new procedure for the construction of 5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine structure using cheaper starting materials has been developed. Introduction of various organic groups on the bismuth atom of 6-*tert*-butyl-5,6,7,12-tetrahydrodibenz[c,f][1,5]azabismocine can be accomplished by organolithium or Grignard reagents, although the latters are sometimes not very suitable depending on the organic groups to be introduced. The X-ray structure determination of 12 new compounds has proved that the eight-membered tetrahydroazabismocine rings are highly flexible and the hypervalent Bi–N bond distances are in good linear relationship against Hammett's σ_m constants of the substituents on the bismuth atom.

4. Experimental

4.1. General

All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques or in a glovebox filled with argon. Et_2O and thf were distilled from Na/benzophenone ketyl. All other anhydrous solvents were purchased from Kanto Chemicals or Aldrich and used as received. $BiCl_3$ was purified by reluxing with $SOCl_2$ and sublimation under vacuum. Magnesium powder (~45 μm, 99.5%) was purchased from Wako Pure Chemical Industries. 3,4-$CH_2O_2C_6H_4MgBr$ and $CH_2{=}C(Me)MgBr$ were purchased from Aldrich and used as received. 2,4,6-$(MeO)_3C_6H_2Li$ was prepared as described in the literature [24]. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol LA500 spectrometer. Chemical shifts given in ppm are referenced to tetramethylsilane for ^1H NMR spectra (0.0 ppm), to solvent signal ($CDCl_3$) for ^{13}C NMR spectra (77.0 ppm) and to $C_6H_5CF_3$ for ^{19}F NMR spectra (−63.72 ppm) and coupling constants were reported in hertz.

4.2. Preparation of $^tBu(2\text{-}ClC_6H_4CH_2)_2N$ (7)

To a mixture of $^tBuNH_2$ (112 g, 1.53 mol), Et_3N (600 ml, 4.3 mol), and NaI (2.81 g, 18.7 mmol) in dmf (700 ml) was added 2-$ClC_6H_4CH_2Cl$ (512 g, 3.18 mol) dropwise under N_2. The mixture was gradually warmed to 85 °C and stirred for 15 h at this temperature. Then the temperature was raised to 120 °C and stirred for 50 h. After cooling to room temperature, Et_2O (1.7 l) and

water (800 ml) were added. Organic layer was separated, dried over Na_2SO_4, and concentrated under vacuum. The residue was passed through a short silica gel column (hexane/EtOAc = 20/1) and then recrystallized from hexane to give **7** as colorless solid (348 g, 71%); m.p. 83–84 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.20 (9H, s), 3.85 (4H, s), 6.96 (2H, dt, J = 1.5, 7.5), 7.04 (2H, dt, J = 1.0, 7.5), 7.13 (2H, dd, J = 7.5, 1.0), 7.52 (2H, dd, J = 7.5, 1.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 26.99 (CH_3), 51.37 (CH_2), 56.07 ($C(CH_3)_3$), 126.03, 127.26, 128.76, 130.83, 132.99, 139.09. Calc. for $C_{18}H_{21}Cl_2N$: C, 67.08; H, 6.57; N, 4.35. Found: C, 67.22; H, 6.54; N, 4.30%.

4.3. Preparation of [^{t}BuN($CH_2C_6H_4$)$_2$BiCl] (**1b**)

From ***3****:* To an Et_2O (250 ml) solution of amine **3** (41.11 g, 100 mmol) was added a hexane solution of ^{n}BuLi (1.55 M, 128 ml, 198 mmol) at −30 °C. The mixture was gradually warmed to room temperature over 3 h and then added to a mixture of $BiCl_3$ (31.76 g, 101 mmol) in Et_2O (750 ml) at −78 °C. The mixture was gradually warmed to room temperature over 8 h and then continued to stir for 7 h at room temperature. Most of the solvent was removed under vacuum and the residue was poured into a mixture of $CHCl_3$ (800 ml) and aqueous NH_4Cl solution (1 M, 400 ml). Organic layer was separated, dried over Na_2SO_4, filtered through Celite. The filtrate was concentrated to one third of the original volume and hexane (500 ml) was added to precipitate **1b** (34.54 g) as colorless crystals. Additional **1b** (5.18 g) was obtained from the residue by silica gel column chromatography (CH_2Cl_2). Total yield: 39.71 g (80%). The purity of **1b** at this stage was ca. 97% by ^{1}H NMR spectroscopy with ca. 3% of bromide **1c**. Recrystallization from CH_2Cl_2/hexane mixture afforded pure **1b**. *From 7*. Magnesium powder (20 g, 0.82 mol) was treated with a tiny piece of I_2 in thf (50 ml) at room temperature. After the disappearance of I_2 color, EtMgCl (2.0 M in thf, 14 ml, 28 mmol) was added and the mixture was heated to 65 °C. To the mixture was added $FeCl_2$ (1.74 g, 13.7 mmol), $MgCl_2$ (0.50 M in thf, 28 ml, 14 mmol), and then amine **7** (88.6 g, 0.275 mol) in thf (100 ml) over 25 min at the same temperature. The mixture was stirred for 1 day at 65 °C and filtered through Celite to remove unreacted magnesium after cooling to room temperature. The solution was added dropwise to a mixture of $BiCl_3$ (72.3 g, 0.229 mol) in thf (800 ml) at −30 °C over 1 h. The mixture was gradually warmed to room temperature and stirred for 1 day. Then the mixture was treated with water (50 ml), filtered, and evaporated. The residue was dissolved in CH_2Cl_2 (700 ml), washed with aqueous HCl (1 M, 200 ml) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in CH_2Cl_2 (300 ml), passed through a silica gel column (300 g) to remove deep brown-colored materials. The eluent was evaporated to give crude **1b**, which was recrystallized from CH_2Cl_2/hexane to give pure **1b** as colorless crystals (46.6 g, 41%); m.p. 265–266 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.29 (9H, s), 4.10 (2H, d, J = 15.5), 4.49 (2H, d, J = 15.5), 7.29 (2H, t, J = 7.5), 7.40 (2H, d, J = 7.5), 7.44 (2H, d, J = 7.5), 8.62 (2H, d, J = 7.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.73 (CH_3), 60.09 ($C(CH_3)_3$), 60.26 (CH_2), 127.47, 128.21, 130.69, 138.24, 151.16 (CCH_2), 170.88 (CBi). Calc. for $C_{18}H_{21}BiClN$: C, 43.60; H, 4.27; N, 2.83. Found: C, 43.31; H, 3.89; N, 2.67%.

4.4. Preparation of [^{t}BuN($CH_2C_6H_4$)$_2$BiF] (**1a**)

To a CH_2Cl_2 solution (5 ml) of phenylbismuth compound **1g** (109 mg, 0.20 mmol) was added a 0.58 M aqueous HF solution (3.5 ml, 2.0 mmol) at room temperature and the resulting mixture was stirred for 3 h at the same temperature. After the addition of 1 M aqueous NH_4F solution (5 ml) and CH_2Cl_2 (10 ml), the organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. NMR analysis of the crude mixture showed quantitative formation of **1a**. Recrystallization from CH_2Cl_2/hexane mixture afforded colorless crystals of **1a** (75 mg, 75%), which was proved to contain one molecule of water per **1a** by the single crystal X-ray analysis; m.p. 171–172 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.29 (9H, s), 4.06 (2H, d, J = 15.5), 4.46 (2H, d, J = 15.5), 7.25 (2H, dt, J = 1.0, 7.5), 7.39 (2H, d, J = 7.5), 7.49 (2H, t, J = 7.5), 8.17 (2H, br, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.50 (CH_3), 59.51 ($C(CH_3)_3$), 60.12 (CH_2), 127.53, 127.93, 129.94, 135.46, 150.91 (CCH_2), 177.57 (CBi). ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ −188.70. Calc. for $C_{18}H_{23}BiFNO$ (**1a** · H_2O): C, 43.47; H, 4.66; N, 2.82. Found: C, 43.43; H, 4.21; N, 2.70%.

4.5. Preparation of [^{t}BuN($CH_2C_6H_4$)$_2$BiBr] (**1c**)

Chloride **1b** (100 mg, 0.202 mmol) and NaBr (500 mg, 4.86 mmol) were dissolved in a mixture of CH_2Cl_2/H_2O (10 ml/10 ml) and stirred for 3 h at room temperature. The organic layer was separated and dried over Na_2SO_4. Removal of the solvent under vacuum gave 99.7 mg (92%) of **1c** as a white solid; m.p. 238–239 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.30 (9H, s), 4.11 (2H, d, J = 15.5), 4.49 (2H, d, J = 15.5), 7.32 (2H, t, J = 7), 7.40 (2H, d, J = 7), 7.43 (2H, t, J = 7), 8.77 (2H, d, J = 7). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.71 (CH_3), 60.12 (CH_2), 60.15 ($C(CH_3)_3$), 127.26, 128.18, 130.91, 140.02, 151.09, 167.43 (CBi). Calc. for $C_{18}H_{21}BiBrN$: C, 40.02; H, 3.92; N, 2.59. Found: C, 40.16; H, 3.77; N, 2.52%.

4.6. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiI] (**1d**)

From 1b: Chloride **1b** (100 mg, 0.202 mmol) and NaI (500 mg, 3.34 mmol) were dissolved in a mixture of CH_2Cl_2/H_2O (10 ml/10 ml) and stirred for 3 h at room temperature. The organic layer was separated and dried over Na_2SO_4. Removal of the solvent under vacuum gave 109 mg (93%) of **1d** as a light yellow solid. ***From 1g***: To a solution of **1g** (2.02 g, 3.75 mmol) in Et_2O (10 ml) was added I_2 (922 mg, 3.63 mmol) at room temperature. The colour of I_2 disappeared quickly and solid precipitated. After stirring at room temperature for 30 min, liquid portion was removed by syringe and the remaining solid was washed with Et_2O (2×10 ml). Recrystallization from toluene gave 1.69 g (79%) of **1d** as light yellow-orange crystals; m.p. > 300 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.32 (9H, s), 4.08 (2H, d, $J = 15.5$), 4.44 (2H, d, $J = 15.5$), 7.36–7.41 (6H, m), 9.00–9.03 (2H, m) ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.83 (CH_3), 59.77 (CH_2), 60.26 ($C(CH_3)_3$), 127.01, 128.28, 131.50, 144.00, 151.04, 161.08 (*C*Bi). Calc. for $C_{18}H_{21}BiIN$: C, 36.81; H, 3.60; N, 2.39. Found: C, 36.80; H, 3.33; N, 2.24%.

4.7. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiC$_6$F$_5$] (**1e**)

To a solution of C_6F_5Li in an Et_2O/hexane mixture, prepared from C_6F_5Br (0.50 ml, 4.0 mmol) and ^{n}BuLi in hexane (1.58 M in hexane, 2.5 ml, 4.0 mmol) in Et_2O (15 ml) at −78 °C, was added **1b** (2.0 g, 4.0 mmol) at −78 °C, and the mixture was stirred overnight with gradual warming to room temperature to form white suspension. The solid was separated by filtration through Celite and the filtrate was concentrated in vacuo. The residual solid was recrystallized from Et_2O (10 ml) to form pure crystals of **1e** (1.09 g, 43%). The separated solid by the above Celite filtration was washed with CH_2Cl_2 to extract remaining **1e**. The CH_2Cl_2 solution was concentrated under vacuum and the resulting solid was recrystallized from Et_2O to give additional **1e** (0.58 g, 23%). Concentration of combined liquid parts of two recrystallizations afforded 0.38 g of solid mainly consisting of **1e**; m.p. 149–152 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.24 (9H, s), 3.99 (2H, d, $J = 15.5$), 4.29 (2H, d, $J = 15.5$), 7.17 (2H, dt, $J = 1.5$, 7.5), 7.27 (2H, dt, $J = 1.0$, 7.5), 7.31 (2H, dd, $J = 1.0$, 7.5), 7.80 (2H, d, $J = 7.5$). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.51, 57.43, 58.38, 127.71, 127.90, 129.55, 135.9–138.3 (a pair of multiplets, *C*–F), 139.84, 139.8–142.1 (a pair of multiplets, *C*–F), 146.7–148.9 (a pair of multiplets, *C*–F), 149.61, 154.49, 169.98. ^{19}F NMR ($CDCl_3$, 469.6 MHz): δ −160.40 (m), −154.86 (t, $J = 19$), −115.08 (m). Calc. for $C_{24}H_{21}BiF_5N$: C, 45.94; H, 3.37; N, 2.23. Found: C, 46.10; H, 3.19; N, 2.13%.

4.8. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$Bi{3,5-(CF$_3$)$_2$-C$_6$H$_3$}] (**1f**)

An Et_2O solution of 3,5-$(CF_3)_2C_6H_3Li$ was prepared by the addition of 1.55 M hexane solution of ^{n}BuLi (10.2 ml, 15.8 mmol) to a solution of 3,5-$(CF_3)_2C_6H_3Br$ (2.8 ml, 16 mmol) in 20 ml of Et_2O at −80 °C and gradual warming of the resulting solution to 10 °C. 18 ml of the above solution was added to a solution of **1b** (4.0 g, 8.1 mmol) in 80 ml of Et_2O at −80 °C. The mixture was stirred overnight with gradual warming to room temperature. ^{1}H NMR analysis of the reaction mixture indicated that **1f** was formed almost quantitatively. After removal of solvent under reduced pressure, the residue was extracted with CH_2Cl_2 (30 ml). The extract was filtered through Celite, which was washed with toluene (10 ml). The combined filtrate was evacuated to reduce the volume to 10 ml to give white precipitates. Removal of the supernatant by decantation, washing the residual solid with hexane (3×15 ml), and drying under vacuum afforded 3.18 g of **1f** (58%). From the supernatant was obtained another crop of **1f** (0.97 g, 18%) by reducing the volume under vacuum; m.p. 218–221 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.23 (9H, s), 3.90 (2H, d, $J = 15.5$), 4.23 (2H, d, $J = 15.5$), 7.12 (2H, td, $J = 7.0$, 1.8), 7.22–7.27 (4H, m), 7.41 (2H, d, $J = 7.5$), 7.86 (1H, s), 8.30 (2H, s). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.35 (CH_3), 56.81 (CH_2), 57.82 ($C(CH_3)_3$), 121.11 (septet, $^3J_{C-F} = 4$), 124.05 (q, $^1J_{C-F} = 273$, CF_3), 127.78, 127.92, 129.30, 131.58 (q, $^2J_{C-F} = 32$, CCF_3), 138.65, 139.49, 149.36 (CCH_2), 153.08 (*C*Bi), 167.84 (*C*Bi). Calc. for $C_{26}H_{24}BiF_6N$: C, 46.37; H, 3.59; N, 2.08. Found: C, 46.46; H, 3.33; N, 2.00%.

4.9. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiPh] (**1g**)

To a suspension of **1b** (10.0 g, 20.2 mmol) in Et_2O (200 ml) was added dropwise a cyclohexane/Et_2O (3/1) solution of PhLi (0.41 M, 50 ml, 21 mmol) over 30 min at −78 °C under nitrogen. After stirring at the same temperature for 30 min, the mixture was allowed to warm to room temperature by removing the cooling bath and stirred for 1 day. ^{1}H NMR analysis of the reaction mixture showed complete consumption of **1b** and nearly quantitative formation of **1g**. The mixture was filtered through Celite and the filtrate was evaporated to remove volatiles. The residue was dissolved in a CH_2Cl_2/hexane (5 ml/40 ml) mixture and filtered through Celite. After removal of volatiles under vacuum, the residual solid was recrystallized by dissolving in a CH_2Cl_2/Et_2O (2.5 ml/25 ml) mixture, reducing the volume of the mixture to ca. 10 ml, and the addition of hexane (10 ml) to give colorless crystal of **1g** (8.81 g, 81%); m.p. 125–126 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.22 (9H, s), 3.85 (2H, d, $J = 15.5$), 4.18

Table 3
Crystal data, data collection and refinement parameters for compounds **1a**–**1e** and **1g**–**1m**

	1a	**1b**	**1c**	**1d**	**1e**	**1g**
Formula	$C_{18}H_{21}BiFN \cdot H_2O$	$C_{18}H_{21}BiClN$	$C_{18}H_{21}BiBrN$	$C_{18}H_{21}BiIN$	$C_{24}H_{21}BiF_5N$	$C_{24}H_{26}BiN$
Formula weight	497.36	495.80	540.26	587.26	627.41	537.46
Crystal size	$0.30 \times 0.15 \times 0.10$	$0.18 \times 0.11 \times 0.04$	$0.25 \times 0.22 \times 0.13$	$0.20 \times 0.20 \times 0.05$	$0.20 \times 0.20 \times 0.15$	$0.55 \times 0.30 \times 0.20$
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)	P_21/n (#14)	P_21/c (#14)	Cc (#9)	$P\bar{1}$ (#2)
a (Å)	10.390(1)	9.8378(9)	9.9307(7)	12.333(1)	9.543(2)	10.176(3)
b (Å)	10.5484(9)	16.072(1)	16.335(1)	9.555(2)	21.834(1)	12.588(5)
c (Å)	9.342(1)	11.3655(8)	11.3634(7)	14.882(2)	11.020(1)	17.295(4)
α (°)	101.75(1)					92.85(3)
β (°)	113.06(1)	109.951(6)	109.914(4)	92.266(9)	105.310(9)	92.15(2)
γ (°)	106.701(9)					109.28(3)
V (Å)	842.2(2)	1689.1(2)	1733.1(2)	1752.4(4)	2214.8(4)	2085(1)
Z	2	4	4	4	4	4
D_{calc} (g cm^{-3})	1.96	1.95	2.07	2.23	1.88	1.71
F(0 0 0)	476.00	944.00	1016.00	1088.00	1200.00	1040.00
μ (Mo Kα) (cm^{-1})	104.60	105.71	124.61	118.00	79.98	84.47
T (K)	173(2)	153(2)	193(2)	153(2)	193(2)	193(2)
Scan type	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	55.0	55.0	55.0	55.0	55.0	55.0
Number of reflections measured	4081	4207	4307	4466	2766	9998
Number of unique reflections	4076 (R_{int} = 0.012)	3871 (R_{int} = 0.022)	3962 (R_{int} = 0.017)	4029 (R_{int} = 0.013)	2692 (R_{int} = 0.089)	9558 (R_{int} = 0.027)
Number of variables	199	212	191	212	302	469
R_1 ($I_0 > 2.0\sigma(I_0)$)	0.042	0.022	0.027	0.022	0.020	0.035
wR_2 (all data)	0.109	0.059	0.083	0.052	0.043	0.134
Goodness-of-fit	1.51	1.02	1.05	1.00	1.04	1.15
Differential peak, hole (e Å^{-3})	4.46, −5.42	1.53, −1.35	2.07, −1.48	1.43, −1.49	1.35, −1.26	1.68, −2.69

	1h	**1i**	**1j**	**1k**	**1l**	**1m**
Formula	$C_{25}H_{26}BiNO_2$	$C_{27}H_{32}BiNO_3$	$C_{21}H_{26}BiN$	$C_{26}H_{26}BiN$	$C_{19}H_{24}BiN$	$C_{24}H_{26}BiNS$
Formula weight	581.47	627.54	501.42	561.48	475.39	569.52
Crystal size	$0.30 \times 0.23 \times 0.15$	$0.22 \times 0.12 \times 0.27$	$0.40 \times 0.30 \times 0.20$	$0.14 \times 0.04 \times 0.02$	$0.35 \times 0.13 \times 0.04$	$0.40 \times 0.40 \times 0.15$
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$Pbca$ (#61)	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a (Å)	9.095(5)	20.816(3)	12.747(3)	9.5606(4)	14.165(1)	20.817(3)
b (Å)	27.273(3)	23.055(2)	13.403(2)	19.7354(9)	9.774(1)	10.533(3)
c (Å)	9.232(2)	10.370(1)	11.398(1)	12.1944(6)	13.995(1)	21.509(2)
α (°)						
β (°)	109.98(3)			111.6300(10)	116.907(4)	115.446(6)
γ (°)						
V (Å)	2152(1)	4976.7(9)	1947.4(5)	2138.8(2)	1727.8(3)	4258.9(9)

Z	4	8	4	4	4	8
D_{calc} (g cm^{-3})	1.81	1.68	1.71	1.74	1.83	1.78
F(0 0 0)	1128.00	2464.00	968.00	1088.00	912.00	2208.00
μ (Mo Kα) (cm^{-1})	82.83	71.00	90.38	82.39	101.80	83.71
T (K)	193(2)	173(2)	193(2)	153(2)	173(2)	193(2)
Scan type	ω	ω–2θ	ω–2θ	ϕ and ω	ω–2θ	ω–2θ
$2\theta_{max}$ (°)	55.4	55.0	54.9	56.5	55.0	55.0
Number of reflections measured	5348	6336	2546	13,818	4372	10,573
Number of unique reflections	4928 (R_{int} = 0.066)	5704 (R_{int} = 0.075)	2525 (R_{int} = 0.057)	5235 (R_{int} = 0.029)	3968 (R_{int} = 0.030)	9762 (R_{int} = 0.015)
Number of variables	262	290	236	279	215	488
R_1 ($I_0 > 2.0\sigma(I_0)$)	0.050	0.028	0.026	0.023	0.029	0.027
wR_2 (all data)	0.139	0.093	0.078	0.058	0.066	0.085
Goodness-of-fit	1.40	0.98	1.01	1.00	1.10	1.09
Differential peak, hole (e Å^{-3})	2.47, −4.86	1.56, −1.91	1.34, −2.51	1.29, −0.65	1.99, −2.08	2.30, −1.86

(2H, d, J = 15.5), 7.06–7.09 (2H, m), 7.18–7.20 (4H, m), 7.39–7.46 (3H, m), 7.59 (2H, d, J = 6.7), 7.84 (2H, dd, J = 7.9, 1.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.32 (*C* H_3), 56.55 (*C*H_2), 57.37 (*C*$(CH_3)_3$), 127.16, 127.23, 127.51, 128.85, 129.74, 139.01, 139.50, 149.13 (*C*CH_2), 152.38 (*C*Bi), 166.08 (*C*Bi). Calc. for $C_{24}H_{26}BiN$: C, 53.63; H, 4.88; N, 2.61. Found: C, 53.73; H, 4.79; N, 2.52%.

4.10. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$Bi{3,4-(CH$_2$O$_2$)-C$_6$H$_3$}] (**1h**)

To a thf solution (100 ml) of **1b** (5.01 g, 10.1 mmol) was added 3,4-$(CH_2O_2)C_6H_3MgBr$ in toluene/thf mixture (1.0 M, 10.1 ml, 10.1 mmol) by syringe at −30 °C. The mixture was stirred for 3 h with gradual warming to room temperature. Heptane (200 ml) was added and the mixture was cooled to −78 °C to settle insoluble magnesium salts, which were removed by filtration. The filtrate was concentrated to one third of the original volume and heptane (100 ml) was added; this operation was repeated three times in order to remove thf and to settle remaining magnesium salts. After the filtration, volatiles were removed under vacuum. The residue was extracted with 100 ml of CH_2Cl_2/hexane (1/4) to remove less soluble bromide **1c**, and the extract was concentrated under vacuum. Recrystallization of the residual solid from CH_2Cl_2/hexane at −25 °C afforded colorless crystal of **1h** (1.20 g, 24%); m.p. 172–173 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.21 (9H, s), 3.84 (2H, d, J = 15), 4.17 (2H, d, J = 15), 5.97 (2H, s), 6.94 (1H, d, J = 7.6), 7.09–7.13 (2H, m), 7.20 (4H, d, J = 4.0), 7.28–7.30 (2H, m), 7.62 (2H, d, J = 7.3). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.30 (*C* H_3), 56.55 (*C*H_2N), 57.37 (*C*$(CH_3)_3$), 100.17 (*C*H_2O), 110.52, 119.04, 127.25, 127.48, 128.88, 132.61, 138.93, 146.97 (*C*OCH_2), 149.14 (*C*CH_2N), 149.98 (*C*OCH_2), 152.61 (*C*Bi), 158.01 (*C*Bi). Calc. for $C_{25}H_{26}BiNO_2$: C, 51.64; H, 4.51; N, 2.41. Found: C, 51.86; H, 4.42; N, 2.32%.

4.11. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$Bi{2,4,6-(MeO)$_3$C$_6$H$_2$}] (**1i**)

To a thf solution (50 ml) of 2,4,6-$(MeO)_3C_6H_2Li$ (2.82 g, 16.2 mmol) was added **1b** (4.01 g, 8.11 mmol) in one portion at −78 °C. The mixture was stirred at the same temperature for 1 h, then gradually warmed to 0 °C over 4 h with stirring and then kept at room temperature overnight. After the addition of hexane (90 ml), insoluble materials were filtered off and the filtrate was washed with water, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Then the residue was subjected to bulb-to-bulb distillation to remove 1,3,5-$(MeO)_3C_6H_3$ under high vacuum and left 4.02 g of a crude mixture consisted of **1i**, **1b** and 1,3,5-$(MeO)_3C_6H_3$ (83/13/4 by weight; at this stage, calculated yield of **1i**

was 66%). Pure **1i** (0.85 g, 17%) was obtained by repeated fractional solvent extraction and fractional precipitation (hexane, hexane/EtOAc mixture, and CH_2Cl_2 were used); m.p. 160–163 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.20 (9H, s), 3.46 (6H, s), 3.87 (2H, d, J = 15.5), 3.89 (3H, s), 4.17 (2H, d, J = 15.5), 6.29 (2H, s), 7.00 (2H, dt, J = 1.5, 7), 7.12–7.18 (4H, m), 7.77 (2H, br d, J = 7.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.42 (C*C*H$_3$), 55.21, 55.24, 55.78, 57.34, 90.92, 126.44, 126.77, 128.01, 140.05, 148.93, 162.77, 165.48. Calc. for $C_{27}H_{32}BiNO_3$: C, 51.68; H, 5.14; N, 2.23. Found: C, 51.82; H, 5.05; N, 2.05%.

4.12. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiCMeCH$_2$] (1j)

To an Et_2O solution (50 ml) of **1b** (4.96 g, 10.0 mmol) was added a thf solution of 2-propenylmagnesium bromide (0.50 M, 25 ml, 12.5 mmol) at −70 °C. After 10 min, the cooling bath was removed and the mixture was stirred for 2 h. The solvent was evaporated and the residue was extracted with a mixture of CH_2Cl_2/hexane (1/1, 30 ml). After removal of the solvent under vacuum, the residue was purified by alumina column chromatography (hexane) to afford **1j** (3.7 g, 74%) as a light yellow solid; m.p. 88.5–90.0 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.15 (9H, s), 2.59 (3H, t, J = 1.5), 3.79 (2H, d, J = 15.4), 4.10 (2H, d, J = 15.4), 5.62 (1H, m), 6.75 (1H, m), 7.18–7.23 (6H, m), 7.87–7.90 (2H, m). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.36 (C(*C*H$_3$)$_3$), 27.75 (CH$_2$=C*C*H$_3$), 56.69 (N*C*H$_2$), 57.21 (*C*(CH$_3$)$_3$), 127.20, 127.75, 128.24 (*C*H$_2$=C), 128.65, 138.54, 149.08 (*C*CH$_2$N), 152.26 (*C*Bi), 172.98 (*C*Bi). Calc. for $C_{21}H_{26}BiN$: C, 50.30; H, 5.23; N, 2.79. Found: C, 50.57; H, 5.20; N, 2.69%.

4.13. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiCCPh] (1k)

An Et_2O/hexane solution of PhC≡CLi was prepared by the addition of ^{n}BuLi (1.56 M hexane solution, 13 ml, 20 mmol) to an Et_2O (24 ml) solution of PhC≡CH (2.2 ml, 20 mmol) at −15 °C and gradual warming to room temperature. The PhC≡CLi solution (20 ml, ca. 10 mmol) was added to an Et_2O (150 ml) solution of **1b** (5.00 g, 10.1 mmol) at −78 °C. Then the mixture was warmed to room temperature over 10 h with stirring. After removal of the solvent under vacuum, the residue was extracted with a CH_2Cl_2/hexane mixture (1/1, 100 ml). The solution was filtered through Celite and evaporated to leave a crude solid product, which was recrystallized from a CH_2Cl_2/hexane mixture to give **1k** (4.90 g, 87%) as colorless crystals; m.p. 147.5–149.0 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.24 (9H, s), 3.83 (2H, d, J = 15.2), 4.25 (2H, d, J = 15.2), 7.23–7.34 (9H, m), 7.57–7.59 (2H, m), 8.81–8.83 (2H, m). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.27 (*C*H$_3$), 56.91 (*C*H$_2$), 57.94 (*C*(CH$_3$)$_3$), 111.14 *C*C$_6$H$_5$), 112.31 *C*CC$_6$H$_5$), 125.39, 127.14, 127.27, 127.63, 128.11, 129.92, 131.84, 140.62, 148.75 (*C*CH$_2$), 154.46 (*C*Bi). Calc. for $C_{26}H_{26}BiN$: C, 55.62; H, 4.67; N, 2.49. Found: C, 55.71; H, 4.67; N, 2.41%.

4.14. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiCH$_3$] (1l)

To an Et_2O solution (100 ml) of **1b** (4.0 g, 8.1 mmol) was added an Et_2O solution of MeLi (1.4 M, 6.0 ml, 8.4 mmol) via a syringe at −78 °C. Then the mixture was allowed to warm to room temperature by removing the cooling bath and stirred for 21 h. The mixture was filtered through Celite under nitrogen and the filtrate was concentrated under vacuum. The residue was dissolved in a CH_2Cl_2/hexane mixture (1/2, 30 ml) and the solution was filtered through Celite under nitrogen. The filtrate was concentrated to ca. 10 ml under vacuum to give **1l** as colorless crystals, which were filtered, washed with hexane and dried under vacuum. 3.4 g (89%); m.p. 119–121 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.18 (9H, s), 1.20 (3H, s), 3.75 (2H, d, J = 15.5), 4.13 (2H, d, J = 15.5), 7.10 (2H, dd, J = 1.0, 7.5), 7.17 (2H, dt, J = 1.0, 7.5), 7.21 (2H, dt, J = 1.0, 7.5), 7.85 (2H, dd, J = 1.0, 7.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 15.60 (Bi–*C*H$_3$), 27.17 (C(*C*H$_3$)$_3$), 56.19 (*C*H$_2$), 57.08 (*C*(CH$_3$)$_3$), 127.10, 127.15, 128.51, 136.48, 144.12, 148.05. Calc. for $C_{19}H_{24}BiN$: C, 48.00; H, 5.09; N, 2.95. Found: C, 48.14; H, 4.96; N, 2.77%.

4.15. Preparation of [^{t}BuN(CH$_2$C$_6$H$_4$)$_2$BiSPh] (1m)

Chloride **1b** (2.97 g, 5.99 mmol) was added into a solution of PhSLi (prepared from PhSH (0.67 ml, 6.6 mmol) and ^{n}BuLi (1.55 M hexane solution, 4.3 ml, 6.6 mmol) in thf (30 ml)). Immediately, the color of the solution turned to orange. After the mixutre was refluxed for 5 h, the solvent was removed under vacuum. The residue was dissolved in CH_2Cl_2, filtered through a filter paper, and the filtrate was evaporated. The residue was passed through alumina (CH_2Cl_2/hexane, 1/5) and the eluate was partially concentrated under vacuum. The addition of hexane to the solution gave **1m** (2.2 g, 64%) as white crystals; m.p. 167–169 °C. ^{1}H NMR ($CDCl_3$, 499.1 MHz): δ 1.25 (9H, s), 3.95 (2H, d, J = 15.2), 4.34 (2H, d, J = 15.2), 7.07 (2H, tt, J = 7.3, 1.4), 7.17–7.21 (2H, m), 7.29–7.34 (4H, m), 7.40–7.43 (2H, m), 7.54–7.56 (2H, m), 8.81–8.83 (2H, m). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 27.50 (*C*H$_3$), 58.38 (*C*H$_2$), 58.88 (*C*(CH$_3$)$_3$), 124.50, 127.58, 127.86, 128.37, 130.39, 134.67, 139.32, 139.96 (*C*S), 150.08 (*C*CH$_2$), 161.84 (*C*Bi). Calc. for $C_{18}H_{21}BiClN$: C, 50.61; H, 4.60; N, 2.46. Found: C, 50.74; H, 4.45; N, 2.36%.

4.16. X-ray crystallography

The crystals were mounted in inert oil (Paratone 8236, Exxon) on glass fibers. Data were collected on a Rigaku AFC7R diffractometer except for **1k**, for which a Bruker Smart Apex CCD area detector diffractometer was used. Crystal data, data collection and refinement parameters for compounds **1a**–**1e** and **1g**–**1m** are given in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis of **1a**–**1e** and **1g**–**1m** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 324070–324081. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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