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Organobismuth(III) and Dibismuthine Complexes Bearing N,N′-Disubstituted 1,8-Diaminonaphthalene Ligand: Synthesis, Structure, and Reactivity

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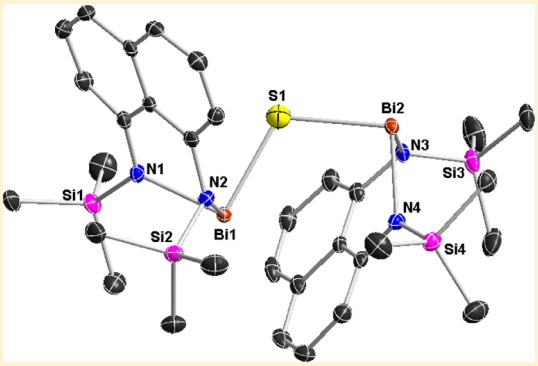
Supporting Information

ABSTRACT: The organobismuth(III) and dibismuthine complexes bearing N,N′-disubstituted 1,8-diaminonaphthalene ligand were prepared. The reaction of $LBiNMe_2$ (**1**) [L = 1,8-$(NSiMe_3)_2C_{10}H_6$] with $ClSiMe_3$ results in the elimination of Me_3SiNMe_2, while PhCCH, Cp*H, and PhOH proceed via $HNMe_2$ elimination and provide the complexes of LBiCl (**2**), LBiCCPh (**3**), LBiCp*(**4**), and LBiOPh (**5**), respectively. Reaction of **1** with $AlMe_3$ in *n*-hexane yields LBiMe (**6**). Compound **1** reacts with diisopropylcarbodiimide and phenyl isocyanate under insertion at the Bi−NMe_2 bond to give the addition products LBi(N-*i*Pr)$_2$CNMe_2 (**7**) and LBiN(Ph)C(O)NMe_2 (**8**). The reactions of **1** with sulfur and $PhSiH_3$ result in the formation of LBi−S−BiL (**9**) and LBi−BiL (**10**), respectively. Compounds **2**−**10** were characterized by elemental analysis, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and X-ray crystallographic studies.



INTRODUCTION

Bismuth compounds are attracting increasing attention due to their application in heterogeneous catalysis,[1] catalysts for organic synthesis,[2] superconducting materials,[3] and also biological activity.[4] Bismuth amides have been used as precursors for metal−organic chemical vapor deposition (MOCVD) of bismuth-containing thin films due to their low Bi−N bond energy.[5] Relatively few bismuth amides with sterically crowded substituents are known. Mason et al. have reported the chelating tridentate triamido complex Bi[N(*t*Bu)-$SiMe_2$]$_3$CH,[6] and Bertrand et al. has reported the diamido-amine complex [$MeN(CH_2CH_2NSiMe_3)_2$]BiCl.[7] Bismuth complexes with chelating amidoamine and diamide ligands have also been reported.[8] An important use of organobismuth compounds is in the preparation of dibismuthines with low-valent bismuth.[9] In addition, they also act as potential precursors for semiconducting bismuth chalcogenides, Bi_2E_3 (E = chalcogen). Several well-defined organobismuth chalcogenides such as $(R_2Bi)_2E$ [R = Mes, E = O, S, Se] have been synthesized and structurally characterized.[10] The low-valent organobismuth compounds which are very air sensitive with weak R-Bi bonds can be synthesized in solution by reduction of Bi(III) species with alkali metals[11] or elimination of hydrogen from secondary bismuthine R_2BiH.[12] In the above-mentioned compound a bulky organic ligand has been used to stabilize the metal center and generate Bi−Bi bonds. In our recent work we have described the insertion of carbon−carbon and carbon−oxygen bonds into the bismuth−nitrogen bond.[13] In this paper we show that N,N′-disubstituted 1,8-diaminonaphthalene, which is a rigid chelating ligand with delocalized π-electron density, is suitable for the preparation and stabilization of organobismuth(III) compounds, bismuthane with low-valent bismuth, organobismuth chalcogenides and also of products by insertion of the diisopropylcarbodiimide and phenyl isocyanate groups into the bismuth−nitrogen bond.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. Compound [1,8-$(NSiMe_3)_2C_{10}H_6$]$BiNMe_2$ (**1**) was prepared by a previously reported method.[13] The terminal NMe_2 group in **1** undergoes substitution by various groups upon treatment with appropriate reagents to afford LBiR (L = 1,8-$(NSiMe_3)_2C_{10}H_6$, R = Cl, CCPh, Cp*, OPh, Me) type of compounds (Scheme 1). When treated with $ClSiMe_3$ in *n*-hexane, **1** undergoes a metathesis reaction in which the amide group was replaced by chloride to afford compound **2**. Organic groups can easily be introduced in **1** by elimination of $HNMe_2$ using acidic reagents. Treatment of **1** with stoichiometric amounts of PhCCH, Cp*H, and PhOH in *n*-hexane results in the formation of LBiCCPh (**3**), LBiCp*(**4**), and LBiOPh (**5**) [L = 1,8-$(NSiMe_3)_2C_{10}H_6$], respectively, under the elimination of $HNMe_2$ as shown in Scheme 1. LBiMe (**6**) can be synthesized by slow addition of $AlMe_3$ in *n*-hexane to the *n*-hexane solution

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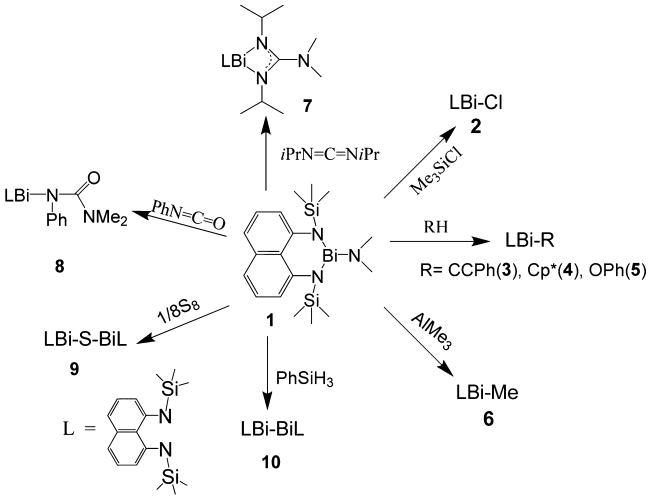
Scheme 1. Preparation of Organobismuth(III) and Dibismuthine Complexes

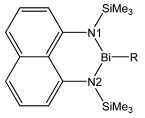


of **1**. The ^{1}H NMR spectrum of each reaction mixture of compounds **2**–**6** shows almost quantitative conversion of the precursors to products, as revealed by the absence of Bi-NMe_2 resonance. The ^{1}H NMR spectra of compounds **2**–**6** in C_6D_6 at room temperature show singlet resonances for $SiMe_3$ groups. The ^{1}H NMR spectrum of **4** displays one resonance at 1.86 ppm which can be attributed to the Me protons of Cp*, whereas the particular BiMe group in **6** resonates as a singlet at 0.43 ppm. The ^{13}C NMR spectrum of **4** reveals two resonances (δ 10.4, 3.3 ppm), which can be assigned to the carbon resonances arising from $SiMe_3$ and Bi–Cp*, respectively. Compound **2** is a red crystalline solid which is soluble in common organic solvents such as toluene and THF, and it is stable in the solid state at room temperature for several months under an inert atmosphere. Organobismuth compounds **3**–**6** are orange crystalline solids which are soluble in toluene, THF, and *n*-hexane. All compounds are air and moisture sensitive and hydrolyze upon exposure to air.

We have recently reported the insertion reaction of **1** with aldehyde, ketone, alkene, and alkyne.[13] Herein, we show the reactivity of **1** toward diisopropylcarbodiimide, phenyl isocyanate, and sulfur (Scheme 1). Reaction of diisopropylcarbodiimide with **1** in *n*-hexane results in the formation of **7**, indicating that one carbodiimide molecule is inserted into the Bi–N bond. In a similar manner *n*-hexane solution of **1** smoothly reacts with phenyl isocyanate at room temperature to afford crystalline **8** in 69% yield under C═N insertion into the Bi–N bond of **1**. Compound **9** is obtained by reaction of **1** with S_8 in *n*-hexane at room temperature. Compounds **7**, **8**, and **9** are orange crystalline solids, which are soluble in organic solvents such as *n*-hexane, THF, and toluene. The ^{1}H NMR spectrum of **7** displays two resonances (δ 1.99, 0.34 ppm) which can be attributed to the NMe_2 and $SiMe_3$ groups, respectively, whereas the CH and CH_3 protons of the *N*-isopropyl groups resonate at 3.93 and 0.94 ppm, respectively. The ^{1}H NMR spectrum of **8** in C_6D_6 exhibits two singlets (δ 2.08, 0.31 ppm) for NMe_2 and $SiMe_3$ groups, respectively. The ^{13}C NMR spectra of **7** and **8** show upfield-shifted resonances of NMe_2 (δ 39.7 and 37.5 ppm, respectively), in comparison to that of **1** (δ 41.9 ppm). An attempt was made to prepare a BiH compound by reaction of **1** with $PhSiH_3$ which was unsuccessful and resulted in the formation of **10** with a Bi–Bi bond formation. Compound **10** is obtained as a red crystalline solid which is air and moisture sensitive but stable in the solid state under an inert atmosphere at room temperature. In the ^{1}H NMR spectrum of **10**, the 18 protons of the Me_3Si group resonate as a singlet (δ 0.15 ppm), and the aromatic protons appear in the range of 7.13–7.22 ppm.

Molecular Structural Details. Single crystals suitable for the X-ray structure of **2** were obtained from a mixture of *n*-hexane/toluene at −30 °C, and those of **3**, **4**, **6**, **7**, **8**, **9**, and **10** were obtained from their saturated solutions in *n*-hexane at −30 °C. Crystallographic data of all compounds are furnished in Table S1 (see Supporting Information [SI]), and important bond parameters are listed in Tables 1 and 2. The coordination geometry around the bismuth atom in compounds **2**, **3**, **4**, and **6** is that of a distorted pyramidal arrangement with a stereochemically active electron lone pair. Compound **2** crystallizes in the tetragonal space group $I\bar{4}$ with one molecule in the asymmetric unit (Figure 1). The Bi–Cl distance (2.4784(6) Å) is shorter than those which have been reported for complexes $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2BiCl$ (2.6086(13) Å)[14] and $[\{HC(Et_2N(CH_2)_2NCMe)_2\}BiCl_2]$ (av 2.7055 Å)[15] but is comparable to that of a characteristic Bi–Cl covalent bond (Σ_{cov}(Bi, Cl) 2.51 Å).[16] Compounds **3** and **6** crystallize in the monoclinic space group $P2_1/n$ with two molecules in the asymmetric unit (Figures 2, 4). The Bi–C bond length (av 2.2115 Å) in **3** is shorter than that in [*t*BuN-

Table 1. Selected Bond Lengths [Å] and Angles [deg] of 2, 3, 4, and 6



	2 R = Cl	3[a] R = PhC≡C	4[a] R = Cp*	6[a] R = Me
Bi–R	2.4784(6)	2.212(3)/2.211(3)	2.62137(10)/2.59054(11)[b]	2.249(3)/2.248(3)
Bi–N1	2.1569(18)	2.142(2)/2.162(2)	2.1854(16)/2.1995(16)	2.1561(19)/2.1541(19)
Bi–N2	2.127(2)	2.145(2)/2.139(2)	2.1568(15)/2.1680(15)	2.1733(19)/2.1771(19)
C≡C		1.202(4)		
N1–Bi–N2	83.88	84.88(8)/84.48(8)	83.46(6)/83.77(6)	83.69(8)/82.47(7)
N1–Bi–R	92.10(6)	89.81/91.65(9)	123.53(4)/123.80(4)[b]	93.32(9)/94.07(8)
N2–Bi–R	95.72(6)	94.91(9)/94.63(9)	118.55(4)/118.55(4)[b]	94.75(9)/95.18(9)

[a]The two numbers in this column refer to two crystallographically independent molecules in the asymmetric unit. [b]Cp* ring centers.

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Table 2. Selected Bond Lengths [Å] and Angles [deg] of 7–10

		cmpd **7**	
Bi(1)–N(1)	2.2356(13)	N(1)–Bi(1)–N(2)	81.51
Bi(1)–N(2)	2.1418(14)	N(3)–Bi(1)–N(4)	56.83(5)
Bi(1)–N(3)	2.2035(14)	N(1)–Bi(1)–N(3)	91.34(5)
Bi(1)–N(4)	2.5259(14)	N(1)–Bi(1)–N(4)	144.97(5)
C(17)–N(3)	1.380(2)	N(2)–Bi(1)–N(3)	96.87(5)
C(17)–N(4)	1.309(2)	N(2)–Bi(1)–N(4)	87.78(5)
C(17)–N(5)	1.369(2)		
		cmpd **8**[a]	
Bi(1)–N(1)	2.1579(14)	N(1)–Bi(1)–N(2)	85.40(6)
Bi(1)–N(2)	2.1183(14)	N(1)–Bi(1)–N(3)	92.88(5)
Bi(1)–N(3)	2.2334(15)	N(2)–Bi(1)–N(3)	97.08(6)
Bi(1)–O(1)	2.6364(13)	C(17)–N(3)–Bi(1)	101.30(11)
C(17)–N(3)	1.373(2)	C(17)–O(1)	1.266(2)
C(17)–N(4)	1.351(2)		
		cmpd **9**[a]	
Bi(1)–N(1)	2.167(2)	N(1)–Bi(1)–N(2)	84.68(8)
Bi(1)–N(2)	2.138(2)	N(3)–Bi(2)–N(4)	84.00(9)
Bi(2)–N(3)	2.144(2)	N(1)–Bi(1)–S(1)	92.10(6)
Bi(2)–N(4)	2.170(2)	N(2)–Bi(1)–S(1)	95.10(6)
Bi(1)–S(1)	2.5386(7)	N(3)–Bi(2)–S(1)	94.96(6)
Bi(2)–S(1)	2.5381(7)	N(4)–Bi(2)–S(1)	98.22(6)
		Bi(1)–S(1)–Bi(2)	112.89(3)
		Bi(1)–S(1)–Bi(2)	113.47(3)
		cmpd **10**	
Bi(1)–N(1)	2.1648(11)	N(1)–Bi(1)–N(2)	84.51(5)
Bi(1)–N(2)	2.1660(12)	N(3)–Bi(2)–N(4)	85.02(4)
Bi(2)–N(3)	2.1621(13)	N(1)–Bi(1)–Bi(2)	89.82(6)
Bi(2)–N(4)	2.1646(11)	N(2)–Bi(1)–Bi(2)	88.87(3)
Bi(1)–Bi(2)	3.0197(2)	N(3)–Bi(2)–Bi(1)	89.95(3)
		N(4)–Bi(2)–Bi(1)	89.19(3)

[a]Only one of the two crystallographically independent molecules in the asymmetric unit.

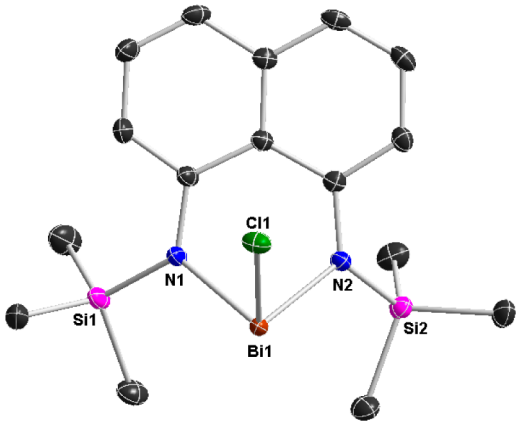

Figure 1. Molecular structure of **2**. Anisotropic displacement parameters are set at the 50% probability level. H atoms are omitted for clarity.

$(CH_2C_6H_4)_2BiCCPh]$ (2.289(4) Å).[17] The Bi–Me distance in **6** (av 2.2485 Å) falls between those found in $[2,6\text{-}(Me_2NCH_2)_2C_6H_3](Me)BiI$ (2.224(10) Å)[14] and $[t\text{BuN}\text{-}(CH_2C_6H_4)_2BiMe]$ (2.264(6) Å).[17] Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit (Figure 3). The Bi–C bond length pattern with one short, two intermediate, and two longer distances (av

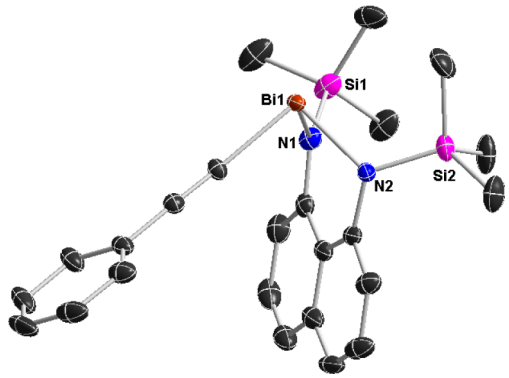

Figure 2. Molecular structure of **3**. Anisotropic displacement parameters are set at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

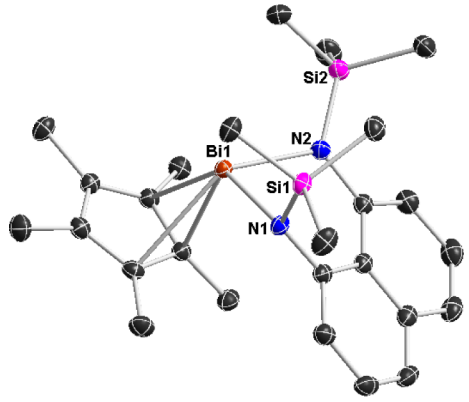

Figure 3. Molecular structure of **4**. Anisotropic displacement parameters are set at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

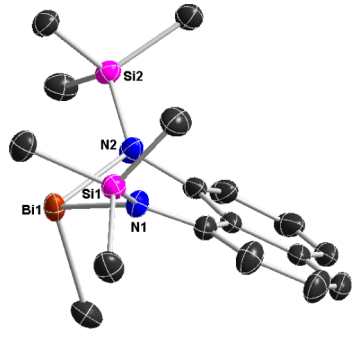

Figure 4. Molecular structure of **6**. Anisotropic displacement parameters are set at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

2.3638, 2.7616, 2.7745, 3.1900, 3.1998 Å) between Cp* and bismuth resembles a scenario between an η^1 and η^3 mode. The Bi–X1A (X1A = centroid of the Cp* ring) distance (2.6059 Å) in **4** is longer than that in $[(C_5HR_4)BiCl_2]_2$ (R = $CHMe_2$) (Bi–X1A, av 2.3495 Å).[18] In compounds **2**, **3**, **4**, and **6**, the Bi–N bond lengths are in the range of 2.127(2) (in **2**) to 2.1995(16) Å (in **4**) and the N–Bi–N angles span from 82.47(7) (in **6**) to 84.88(8)° (in **3**), which are comparable to those observed in our previously reported compounds.[13]

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The coordination geometry around the bismuth atom in compounds **8**–**10** is distorted pyramidal, whereas in **7** the bismuth atom is tetracoordinate in an irregular trigonal–pyramidal environment. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 5), while compound **8** crystallizes in

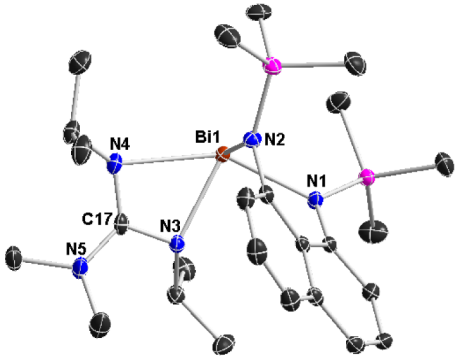

Figure 5. Molecular structure of **7**. Anisotropic displacement parameters are set at the 50% probability level. H atoms are omitted for clarity.

the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit (Figure 6). The bismuth atom in **7** is

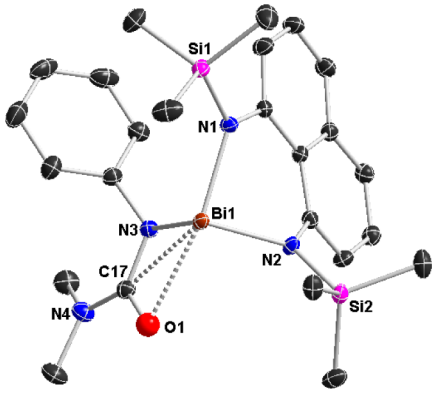

Figure 6. Molecular structure of **8**. Anisotropic displacement parameters are set at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

coordinated to two nitrogen atoms of the anionic ligand and to two nitrogen atoms of the carbodiimide unit. The C–N bond distances associated with the central sp^2 carbon of the carbodiimide species are almost equal and are considerably shorter than a typical C–N single bond, suggesting that the three C–N bonds possess a partial double bond character (C(17)–N(3) = 1.380(2), C(17)–N(4) = 1.309(2), and C(17)–N(5) = 1.369(2) Å). Among these, the C(17)–N(4) bond of 1.309(2) Å is appreciably shorter compared to the other two bond distances. The difference in the bond lengths of C(17)–N(3) and C(17)–N(4) is further supported by the observation that the N(4)–Bi(1) bond (2.5259(14) Å) is longer compared to the N(3)–Bi(1) bond (2.2035(14) Å), indicating the weak coordinating character of the N(4)–Bi(1) bond. In **8** both the N–C (av 1.384 and 1.352 Å) and C–O (av 1.255 Å) bond distances of the ureato fragments are in the range of partial double bonds, indicating that the π electrons of the ureato fragments are delocalized in the NC(N)O core. Additionally, the intramolecular coordination between bismuth and oxygen may play an important role for the stability of this compound. Compound **9** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the asymmetric unit (Figure 7). In **9** the bismuth atoms are bound by a sulfur atom

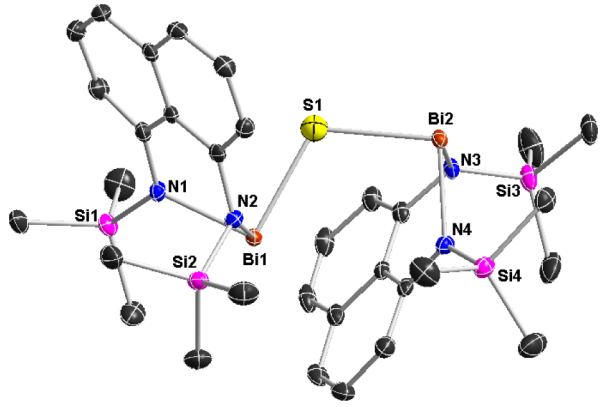

Figure 7. Molecular structure of **9**. Anisotropic displacement parameters are set at the 50% probability level. Only one of the two crystallographically independent molecules is shown. H atoms are omitted for clarity.

constituting a bent Bi(μ-S)Bi core with Bi–S–Bi bond angle of av 113.18°. The bismuth–sulfur distances in **9** (av 2.5383 Å) are similar to those in $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Bi]_2S$ (2.5558(17) Å)[10] and $(Mes_2Bi)_2S$ (av 2.5325 Å),[19] whereas the Bi(μ-S)Bi angle of 113.18° in **9** is considerably larger when compared with those of the latter compounds (98.17(8)°, 98.7(2)°). Two crystallographically independent molecules of **9** in the asymmetric unit are showing an intermolecular secondary Bi–S contact with Bi3–S1 distance of 3.186 Å (see Figure S1 in the SI). Compound LBi–BiL (**10**) crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 8). The N,N′-disubstituted 1,8-

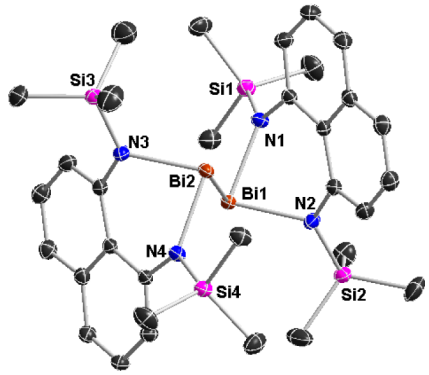

Figure 8. Molecular structure of **10**. Anisotropic displacement parameters are set at 50% probability level. H atoms are omitted for clarity.

diaminonaphthalene ligands of **10** are in a trans conformation to each other, and the N–Bi–Bi angles lie in the range of av 89.34° and av 89.57°. The Bi–Bi bond distance of 3.0197(2) Å corresponds to a normal bismuth–bismuth single bond as found in $(Me_3Si)_4Bi_2$ (3.035(3) Å)[20] or R_4Bi_4 (R = $(Me_3Si)_2CH$; av 3.005 Å).[21]

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A notable feature of some of the bismuth compounds reported in this contribution is their close bismuth−arene (Bi−arene) contacts which are either intermolecular or intramolecular. In compound **9**, each molecule in the asymmetric unit possesses one bismuth atom that has close proximity to one of the aromatic rings of the ligand in the same molecule, and this leads to an intramolecular Bi−arene interaction (Figure S2 in the SI). Moreover, one of the bismuth atoms of one molecule interacts with the aromatic ring of the second molecule resulting in an intermolecular Bi−arene contact. Such weak interactions obviously have considerable influence on the coordination environments of bismuth centers, molecular geometries, and crystal properties. A recent work by Auer and Mehring demonstrated the property of such Bi−arene interactions in the triorganobismuth compound $[Bi(CH_2C_6H_4Cl)_3]_2$ in which Bi−arene π-coordination and $\pi-\pi$ stacking interactions with distances of 3.659 Å ($Bi-arene_{centroid}$) and 3.869 Å (arene centroids) were observed.[22] In compound **9**, Bi1, Bi3, and Bi4 are at a distance of 3.173, 3.454, and 3.220 Å, respectively, from the centroids of the arene rings with which they interact. Therefore it is expected that Bi−arene interactions present in this compound have similar properties of Bi−arene π-coordination as demonstrated by Auer and Mehring. Compounds **2**, **3**, and **6** also exhibit weak intermolecular Bi−arene interactions, and these are demonstrated in Figures S3, S4, and S5, respectively (see the SI).

CONCLUSION

Organobismuth(III) and dibismuthine complexes bearing the N,N′-disubstituted 1,8-diaminonaphthalene ligand were synthesized and structurally characterized. Reaction of $LBiNMe_2$ (**1**) [L = 1,8-$(NSiMe_3)_2C_{10}H_6$] with $ClSiMe_3$, PhCCH, Cp*H, and PhOH in *n*-hexane resulted in the formation of LBiCl (**2**), LBiCCPh (**3**), LBiCp* (**4**), and LBiOPh (**5**), respectively. $LBiNMe_2$ reacts with $AlMe_3$ in *n*-hexane to afford LBiMe (**6**). The treatment of $LBiNMe_2$ with diisopropylcarbodiimide and phenyl isocyanate resulted in the insertion reactions at the Bi−NMe_2 bond of **1** to afford the addition products $LBi(N-iPr)_2CNMe_2$ (**7**) and $LBiN(Ph)C(O)NMe_2$ (**8**), respectively. In the reaction of **1** with sulfur, LBi−S−BiL (**9**) was produced. When $PhSiH_3$ was treated with $LBiNMe_2$, elimination of $HNMe_2$ occurred to give LBi−BiL (**10**).

EXPERIMENTAL SECTION

General Comments. All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a glovebox. The solvents were purified according to conventional procedures and were freshly distilled prior to use. PhC≡CH, $ClSiMe_3$, $PhSiH_3$, *N*,*N*′-diisopropylcarbodiimide, and phenylisocyanate were purchased from Aldrich. NMR spectra were recorded either on a Bruker Avance DPX 200 or Bruker Avance DRX 500 NMR spectrometer and were referenced to the deuterated solvent in the case of the ^1H and ^{13}C NMR spectra. ^{29}Si NMR spectra were referenced to $SiMe_4$. All NMR measurements were carried out at room temperature. Melting points were measured in sealed glass tubes on a Büchi B-540 melting point apparatus and are uncorrected. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen, Germany. [1,8-$(NSiMe_3)_2C_{10}H_6$]$BiNMe_2$ (**1**) was prepared according to literature procedure.[13] For X-ray structure analysis single crystals were selected from the Schlenk flasks under an argon atmosphere and covered with perfluorinated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using the X-TEMP2.[23] An appropriate crystal was selected using a polarizing microscope, mounted on the tip of a glass fiber, fixed to a goniometer head, and shock cooled by the crystal cooling device.[24]

For **2** and **9**, data were collected on a Bruker Apex II Ultra at 100 K (Mo Kα radiation, λ = 71.073 pm; multilayer mirror optics), and for **3**, **6**, **7**, **8**, and **10** data were collected on a Bruker APEX II Quazar at 100 K (Mo Kα radiation, λ = 71.073 pm; multilayer mirror optics).[25] The data were integrated with SAINT,[26] and a semi-empirical absorption correction from equivalents was applied.[27] The structures were solved by direct methods (SHELXS) and refined on F^2 using the full-matrix least-squares methods of SHELXL.[28] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms bonded to sp^2 (sp^3) carbon atoms were assigned ideal positions and refined using a riding model with U_{iso} constrained to 1.2 (1.5) times the U_{eq} value of the parent carbon atom. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre; the CCDC numbers are listed in Table S1 in the SI.

Preparation of [1,8-$(NSiMe_3)_2C_{10}H_6$]BiCl (2). To a stirred solution of **1** (0.7 g, 1.26 mmol) in *n*-hexane (30 mL) was added 0.16 mL (1.26 mmol) of $ClSiMe_3$ at −10 °C. The reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed in vacuo, and the resulting solid was washed with cold *n*-hexane (20 mL) to give a red crystalline solid. The product was recrystallized from a toluene/*n*-hexane mixture (2:1) to yield red crystals. Yield: 0.47 g (69%); mp 163 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.41 (d 2H), 7.28 (t, 2H), 7.16 (d 2H), 0.17(s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 146.53, 138, 131.7, 126.8, 121.1, 116.3, 2.65. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 4.6. Anal. Calcd for $C_{16}H_{24}BiClN_2Si_2$: C, 35.26; H, 4.44; N, 5.14. Found: C, 34.92; H, 4.21; N 5.09.

Preparation of [1,8-$(NSiMe_3)_2C_{10}H_6$]BiC≡CPh (3). To a stirred solution of **1** (0.7 g, 1.26 mmol) in *n*-hexane (30 mL) was added 0.14 mL (1.26 mmol) of phenyl acetylene at −10 °C. The reaction mixture was warmed to room temperature and stirred overnight. Then the mixture was concentrated and stored at −30 °C in a freezer. Orange crystals were obtained after two days. Yield: 0.41 g (54%); mp 98 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.48−7.51 (m, 2H), 7.24−7.31 (m, 3H), 6.85−6.89 (m, 2H), 6.74−6.77 (m, 3H), 0.23 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 150.1, 138, 134, 131.9, 126.4, 123.7, 120.6, 116.2, 111.9, 3.1. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 4.1. Anal. Calcd for $C_{24}H_{29}BiN_2Si_2$: C, 47.2; H, 4.79; N, 4.59. Found: C, 46.66; H, 4.80; N, 4.42.

Preparation of [1,8-$(NSiMe_3)_2C_{10}H_6$]BiCp* (4). The *n*-hexane solution (30 mL) of **1** (0.28 g, 0.5 mmol) was added to an *n*-hexane solution (20 mL) of Cp*H (0.07 g, 0.5 mmol) at room temperature. The reaction mixture was stirred overnight, then concentrated and stored at −30 °C in a freezer to obtain orange crystals. Yield: 0.22 g (68%); mp 148 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.23−7.41 (m, 6H), 1.86 (s, 315H), 0.27 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 148.8, 138.9, 130.3, 127.8, 126.6, 124.5, 120.3, 117.7, 10.4, 3.3. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 1.14. Anal. Calcd for $C_{26}H_{39}BiN_2Si_2$: C, 48.43; H, 6.10; N, 4.34. Found: C, 47.94; H, 5.98; N, 4.45.

Preparation of [1,8-$(NSiMe_3)_2C_{10}H_6$]BiOPh (5). *n*-Hexane (40 mL) was added to the mixture of **1** (0.7 g, 1.26 mmol) and phenol (0.12 g, 1.26 mmol) at room temperature and stirred overnight. After filtration the resulting solution was concentrated and stored at −30 °C in a freezer to obtain a yellow solid. Yield: 0.48 g (64%); mp 149 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.41 (d, 2H), 7.24 (t, 2H), 6.94−7.02 (m, 4H), 6.65 (t, 1H), 6.29 (d, 2H), 0.11 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 159.2, 146.5, 138.2, 130.5, 126.7, 122.1, 120.8, 120.5, 117.1, 2.4. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 3.11. Anal. Calcd for $C_{22}H_{29}BiN_2OSi_2$: C, 43.85; H, 4.85; N, 4.65. Found: C, 43.65; H, 4.91; N, 4.65.

Preparation of [1,8-$(NSiMe_3)_2C_{10}H_6$]BiMe (6). $AlMe_3$ (0.8 mL, 1.6 mmol, 2.0 M in *n*-hexane) was added to an *n*-hexane (50 mL) solution of **1** (0.88 g, 1.6 mmol) at −78 °C. The mixture was stirred for 1 h at this temperature and then was allowed to attain room temperature, and stirring was continued for 12 h. The mixture was concentrated and stored at −30 °C in a freezer to give a yellow microcrystalline solid. Yield: 0.31 g (37%); mp 109 °C. ^1H NMR

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(500.13 MHz, C_6D_6): δ 7.23−7.31 (m, 4H), 7.44−7.48 (m, 2H), 0.43 (s, 3H), 0.28 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 149.2, 138.4, 131.2, 126.2, 120.7, 117.9, 3.3, −9.6. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 3.7. Anal. Calcd for $C_{17}H_{27}BiN_2Si_2$: C, 38.92; H, 5.19; N, 5.34. Found: C, 38.75; H, 5.11; N, 5.46.

Preparation of [1,8-(NSiMe$_3$)$_2$C$_{10}$H$_6$]Bi(N*i*Pr)$_2$CNMe$_2$ (7). To a stirred solution of *N*,*N*′-diisopropylcarbodiimide (0.1 g, 0.79 mmol) in *n*-hexane (20 mL) was added a solution of **1** (0.42 g, 0.76 mmol) in *n*-hexane (20 mL). The reaction was allowed to stir at room temperature for 12 h. Then the mixture was concentrated and stored at −30 °C in a freezer to obtain yellow crystals. Yield: 0.4 g (78%); mp 116 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.11−7.43 (m, 6H), 3.93 (sept, 2H), 1.99 (s. 6H), 0.94 (d, 12H), 0.34 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 166.5, 150.2, 138.2, 132.4, 126.2, 119.8, 117.3, 47.3, 39.7, 24.9, 2.7. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 0.21. Anal. Calcd for $C_{25}H_{44}BiN_5Si_2$: C, 44.17; H, 6.52; N, 10.30. Found: C, 44.38; H, 6.41; N, 10.42.

Preparation of [1,8-(NSiMe$_3$)$_2$C$_{10}$H$_6$]BiNPhCONMe$_2$ (8). To a stirred solution of phenylisocyanate (0.19 g, 1.6 mmol) in *n*-hexane (20 mL) was added a solution of **1** (0.88 g, 1.6 mmol) in *n*-hexane (20 mL). The reaction was allowed to stir at room temperature for 12 h. Then the mixture was concentrated and stored at −30 °C in a freezer to obtain yellow crystals. Yield: 0.73 g (69%); mp 151 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.31−7.36 (m, 2H), 7.16−7.22 (m, 2H), 6.97−7.03 (m, 2H), 6.84−6.91 (m, 2H), 6.59−6.66 (m, 1H), 6.18−6.23 (m, 2H), 2.08 (s, 6H), 0.31 (s, 18H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 148.2, 144.3, 138.4, 130.6, 126.5, 126, 123.8, 119.5, 115.5, 37.5, 2.71. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 2.93. Anal. Calcd for $C_{25}H_{35}BiN_4OSi_2$: C, 44.63; H, 5.24; N, 8.33. Found: C, 44.99; H, 5.51; N, 8.26.

Preparation of {[1,8-(NSiMe$_3$)$_2$C$_{10}$H$_6$]Bi}$_2$S (9). *n*-Hexane (50 mL) was added to the mixture of **1** (0.41 g, 0.75 mmol) and sulfur (0.024 g, 0.75 mmol) at room temperature and stirred for 2 days. After filtration, the resulting solution was concentrated and stored at −30 °C in a freezer to obtain yellow crystals. Yield: 0.48 g (61%); mp 130 °C. ^1H NMR (500.13 MHz, C_6D_6): δ 7.11−7.44 (m, 10H), 6.68−6.72 (m, 2H), 0.18 (s, 36H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 149.3, 144.5, 138.2, 132.8, 125.9, 121.2, 120, 116.6, 116.1, 3.06. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 2.86. Anal. Calcd for $C_{32}H_{48}Bi_2N_4SSi_4$: C, 36.57; H, 4.60; N, 5.33; S, 3.05. Found: C, 36.75; H, 4.51; N, 5.41; S, 3.21.

Preparation of {[1,8-(NSiMe$_3$)$_2$C$_{10}$H$_6$]Bi}$_2$ (10). The *n*-hexane solution (30 mL) of **1** (1.0 g, 1.8 mmol) was added to an *n*-hexane solution (20 mL) of $PhSiH_3$ (0.2 g, 1.85 mmol) at −30 °C. The reaction mixture was warmed to room temperature and stirred for an additional 12 h. Then the mixture was concentrated and stored at −30 °C in a freezer to obtain red crystals of **10**. Yield (1.1 g 60%); mp 245 °C; ^1H NMR (500.13 MHz, C_6D_6): δ 7.13−7.22 (m, 12H), 0.15 (s, 36H). ^{13}C NMR (125.8 MHz, C_6D_6): δ 155.7, 138.4, 137.1, 124.9, 120.4, 115.3, 3.7. ^{29}Si NMR (59.6 MHz, C_6D_6): δ 6.69. Anal. Calcd for $C_{32}H_{48}Bi_2N_4Si_4$: C, 37.72; H, 4.75; N, 5.50. Found: C, 37.86; H, 4.78; N, 5.41.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files and a table giving crystal data and details of the structure solution and refinement for **2**, **3**, **4**, **6**, **7**, **8**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) (a) Roggan, S.; Limberg, C.; Ziemer, B. *Angew. Chem.* **2005**, *117*, 5393−5397; *Angew. Chem., Int. Ed.* **2005**, *44*, 5259−5262. (b) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133−163. (c) Aghapoor, K.; Ebadi-Nia, L.; Mohsenzadeh, F.; Mohebi Morad, M.; Balavar, Y.; Darabi, H. R. *J. Organomet. Chem.* **2012**, *708*−*709*, 25−30.

(2) (a) Shimada, S.; Yamazaki, O.; Tanaka, T.; Rao, M. L. N; Suzuki, Y.; Tanaka, M. *Angew. Chem.* **2003**, *115*, 1889−1892; *Angew. Chem., Int. Ed.* **2003**, *42*, 1845−1848. (b) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley-Interscience: New York, 1970. (c) Gaspard-Iloughmane, H.; Le Roux, C. *Eur. J. Org. Chem.* **2004**, 2517−2532. (d) Suzuki, H.; Ikegami, T.; Matano, Y. *Synthesis* **1997**, 249−267. (e) Fan, A.; Jaenicke, S.; Chuah, G.-K. *Org. Biomol. Chem.* **2011**, *9*, 7720−7726.

(3) (a) Dagani, R. *Chem. Eng. News* **1987**, *65*, 41−49. (b) Reshak, A. H.; Kamarudin, H.; Auluck, S. *J. Alloys Compd.* **2011**, *509*, 9685−9691.

(4) (a) Silvestru, C.; Breunig, H. J.; Althaus, H. *Chem. Rev.* **1999**, *99*, 3277−3328. (b) Summers, S. P.; Abboud, K. A.; Farrah, S. R.; Palenik, G. J. *Inorg. Chem.* **1994**, *33*, 88−92. (c) Klapötke, T. *J. Organomet. Chem.* **1987**, *331*, 299−307. (d) Sun, H.; *Ed., Biological Chemistry of Arsenic, Antimony, and Bismuth*; Wiley: United Kingdom, 2011.

(5) Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Green, M. E.; Hockless, D. C. R.; Norman, N. C. *Inorg. Chem.* **1991**, *30*, 4680−4682.

(6) Mason, M. R.; Phulpagar, S. S.; Mashuta, M. S.; Richardson, J. F. *Inorg. Chem.* **2000**, *39*, 3931−3933.

(7) Fauré, J.-L.; Gornitzká, H.; Réau, R.; Stalke, D.; Bertrand, G. *Eur. J. Inorg. Chem.* **1999**, 2295−2299.

(8) (a) Raston, C. L.; Skelton, B. W.; Tolhurst, V.-A.; White, A. H. *Polyhedron* **1998**, *17*, 935−942. (b) Caminade, A.-M.; Veith, M.; Huch, V.; Malisch, W. *Organometallics* **1990**, *9*, 1798−1802.

(9) Balazs, L.; Breunig, H. J. *Coord. Chem. Rev.* **2004**, *248*, 603−621.

(10) Breunig, H. J.; Königsmann, L.; Lork, E.; Nema, M.; Philipp, N.; Silvestru, C.; Soran, A.; Varga, R. A.; Wagner, R. *Dalton Trans.* **2008**, 1831−1842.

(11) (a) Breunig, H. J.; Müller, D. *Z. Naturforsch.* **1983**, *38b*, 125−127. (b) Ashe, A. J., III; Ludwig, E. G. *Organometallics* **1982**, *1*, 1408−1410.

(12) (a) Balazs, L.; Breunig, H. J.; Lork, E. *Z. Naturforsch.* **2005**, *60b*, 180−182. (b) Balazs, G.; Breunig, H. J.; Lork, E. *Organometallics* **2002**, *21*, 2584−2586.

(13) Nekoueishahraki, B.; Sarish, S. P.; Roesky, H. W.; Stern, D.; Schulzke, C.; Stalke, D. *Angew. Chem.* **2009**, *121*, 4587−4590; *Angew. Chem., Int. Ed.* **2009**, *48*, 4517−4520.

(14) Soran, A. P.; Silvestru, C.; Breunig, H. J.; Balazs, G.; Green, J. C. *Organometallics* **2007**, *26*, 1196−1203.

(15) Pineda, L. W.; Jancik, V.; Nembenna, S.; Roesky, H. W. *Z. Anorg. Allg. Chem.* **2007**, *633*, 2205−2209.

(16) Emsley, J. *Die Elemente*; Walter de Gruyter: Berlin, 1994.

(17) Shimada, S.; Yamazaki, O.; Tanaka, T.; Yohichi, S.; Tanaka, M. *J. Organomet. Chem.* **2004**, *689*, 3012−3023.

(18) Sitzmann, H.; Wolmershäuser, G. *Z. Anorg. Allg. Chem.* **1999**, *625*, 2103−2107.

(19) Breunig, H. J.; Ebert, K. H.; Schulz, R. E.; Wieber, M.; Sauer, I. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 735−737.

(20) Mundt, O.; Becker, G.; Rössler, M.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1983**, *506*, 42−58.

(21) Breunig, H. J.; Rösler, R.; Lork, E. *Angew. Chem.* **1998**, *110*, 3361−63; *Angew. Chem., Int. Ed.* **1998**, *37*, 3175−3177.

(22) Auer, A. A.; Mansfeld, D.; Nolde, C.; Schneider, W.; Schürmann, M.; Mehring, M. *Organometallics* **2009**, *28*, 5405−5411.

(23) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615−619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171−178.

(24) Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465−468.
(25) Schulz, T.; Meindl, K.; Leusser, D.; Stern, D.; Graf, J.; Michaelsen, C.; Ruf, M.; Sheldrick, G. M.; Stalke, D. *J. Appl. Crystallogr.* **2009**, *42*, 885−891.
(26) *SAINT*, v7.68A; *Bruker APEX*, v2009.9; Bruker AXS Inst. Inc.: Madison, WI, 2009.
(27) Sheldrick, G. M. *SADABS 2008/1/TWINABS 2008/1* ; Göttingen, Germany, 2008.
(28) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−120.