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Article

Isomers of a Dibismuthane, $R_2Bi–BiR_2$ [R = 2,6-$(Me_2NCH_2)_2C_6H_3$], and Unusual Reactions with Oxygen: Formation of $[R_2Bi]_2(O_2)$ and R′R″Bi [R′ = 2-(Me_2NCH_2)-6-{$Me_2N(O)CH_2$}C_6H_3; R″ = 2-(Me_2NCH_2)-6-{O(O)C}C_6H_3]

Lucia Balazs,[†] Hans J. Breunig,*[,†] Enno Lork,[†] Albert Soran,[‡] and Cristian Silvestru*[,‡]

Universität Bremen, Fachbereich 2, D-28334 Bremen, Germany, and Facultatea de Chimie si Inginerie Chimica, Universitatea "Babes-Bolyai" Cluj-Napoca, RO-400028 Cluj-Napoca, Romania

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$R_2Bi–BiR_2$ [**1**; R = 2,6-$(Me_2NCH_2)_2C_6H_3$], a dibismuthane that exists in different forms in the crystalline state, reacts in air with the formation of the peroxide $[R_2Bi]_2(O_2)$ (**2**) and partial oxidation of the pendant (dimethylamino)methyl groups, yielding the mononuclear bismuth complex R′R″Bi (**3**) [R′ = 2-(Me_2NCH_2)-6-{$Me_2N(O)CH_2$}C_6H_3; R″ = 2-(Me_2NCH_2)-6-{O(O)C}C_6H_3].

Introduction

Tetraorganodibismuthanes, $R_2Bi-BiR_2$ (R = alkyl, aryl), are air-sensitive compounds, and many alkyl derivatives are even self-igniting when exposed to air.[1] It is, however, possible to moderate the reactivity with oxygen, and several reports on controlled oxidation reactions of dibismuthanes have appeared.[2−7] Although as an initial step the insertion of dioxygen into the Bi−Bi bond was proposed, attempts failed to prove the existence of bis(diorganobismuthyl) peroxide.[2] Only monoxides of the type $(R_2Bi)_2O$,[5−7] or rearrangement products Bi_2O_3 and R_3Bi,[2,3] were isolated, and bis(dimesitylbismuthyl) oxide was characterized by X-ray crystallography.[5,6] Dibismuthanes with known crystal structures include $R_2Bi-BiR_2$ [R = Ph,[2] $(Me_3Si)_2CH$,[8] 2-$(Me_2NCH_2)C_6H_4$,[9] 2,4,6-$Me_3C_6H_2$,[10] Me_3Si;[11] R_2 = $(HC{=}CMe)_2$[12]] with Bi−Bi bond lengths ranging from 2.990 to 3.066 Å.[13]

We report here the synthesis, structures, and reactions of $R_2Bi-BiR_2$ [**1**; R = 2,6-$(Me_2NCH_2)_2C_6H_3$], a tetraaryldibismuthane with protection by eight pendant amino groups. Compound **1** reacts with air to form the peroxide $[R_2Bi]_2(O_2)$ (**2**) and R′R″Bi [**3**; R′ = 2-(Me_2NCH_2)-6-{$Me_2N(O)CH_2$}C_6H_3; R″ = 2-(Me_2NCH_2)-6-{O(O)C}C_6H_3], a mononuclear bismuth complex where the pendant Me_2NCH_2 groups are partially oxidized.

Experimental Section

General Procedures. All syntheses and manipulations of the air-sensitive compounds were carried out under argon using standard Schlenk techniques. All solvents were dried and freshly distilled under argon before use. The ligand 1,3-$(Me_2NCH_2)_2C_6H_4$ was synthesized according to a literature procedure.[14] All other reagents were commercially available. The NMR spectra were run on a Bruker Avance DRX 600 instrument for R_2BiCl and a Bruker DPX 200 instrument for the rest of compounds. Chemical shifts are reported in δ units (ppm) referenced to C_6D_5H (7.15 ppm, ^1H) and

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* To whom correspondence should be addressed. E-mail: breunig@chemie.uni-bremen.de (H.J.B.), cristi@chem.ubbcluj.ro (C.S.). Tel: (+49)421-2182266 (H.J.B.), (+40)264-593833 (C.S.). Fax: (+49)-421-2184042 (H.J.B.), (+40)264-590818 (C.S.).

[†] Universität Bremen.

[‡] Universitatea "Babes-Bolyai" Cluj-Napoca.

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Table 1. Summary of Single-Crystal X-ray Diffraction Data for Compounds **1**−**3**

	1a·$CH_3C_6H_5$	**1b/c**·Et_2O	**2**·Et_2O	**3**
formula	$C_{48}H_{76}Bi_2N_8 \cdot C_7H_8$	$C_{48}H_{76}Bi_2N_8 \cdot C_2H_5O_{0.5}$	$C_{52}H_{86}Bi_2N_8O_3$	$C_{22}H_{30}BiN_3O_3$
fw	1275.26	1220.19	1289.25	593.47
T/K	173(2)	173(2)	173(2)	173(2)
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a/Å	12.276(2)	11.242(2)	11.446(3)	11.451(2)
b/Å	21.942(4)	21.154(4)	12.012(5)	11.096(1)
c/Å	21.119(4)	22.509(4)	23.542(6)	17.588(2)
α/deg	90	95.49(2)	85.28(3)	90
β/deg	103.55(3)	90.68(1)	77.77(1)	94.53(1)
γ/deg	90	98.20(1)	62.15(2)°	90
V/Å^3	5530.3(17)	5272.1(17)	2796.4(15)	2227.8(5)
Z	4	2	2	4
D_c/g cm^{-1}	1.522	1.540	1.531	1.769
μ(Mo Kα)/mm^{-1}	6.396	6.704	6.330	7.941
R1 [$I > 2\sigma(I)$]	0.0387	0.0647	0.0439	0.0508
wR2	0.0902	0.1134	0.1004	0.0719
largest diff peak and hole/e Å^{-3}	2.085/−1.163	1.685/−1.780	2.095/−2.304	0.885/−0.839
CCDC no.	284976	284977	284974	284975

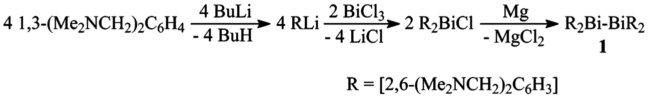
C_6D_6 (128.0 ppm, ^{13}C). Mass spectrometry (MS) and IR spectra were recorded on a Finnigan MAT 8222 spectrometer and a Fourier transform IR Spektrum 1000 instrument, respectively.

Synthesis of [2,6-(Me_2NCH_2)$_2$$C_6H_3$]$_4$$Bi_2$ (1). Butyllithium (16.3 mL, 15% solution in hexane, 26 mmol) was added dropwise to a solution of 1,3-(Me_2NCH_2)$_2$$C_6H_4$ (5.2 g, 27 mmol) in 60 mL of hexane. The reaction mixture was stirred under reflux for 12 h, and removal of the solvent in a vacuum gives RLi as a white-orange powder, which is dissolved in 80 mL of diethyl ether. This solution was added dropwise at −80 °C to a solution of $BiCl_3$ (4.1 g, 13 mmol) in 100 mL of diethyl ether. The mixture was warmed to room temperature, stirred for 12 h, and then filtered. Removal of the solvent gives 6.15 g (75%) of R_2BiCl [R = 2,6-(Me_2NCH_2)$_2$$C_6H_3$] as a white solid [mp 155 °C; ^{1}H NMR (600 MHz, 25 °C, $CDCl_3$, TMS) δ 2.18 (12H, s, CH_3), 3.62 (4H, s, CH_2), 7.27 (1H, t, C_6H_3, $^3J_{HH} = 7.5$ Hz), 7.38 (2H, d, C_6H_3, $^3J_{HH} = 7.4$ Hz); MS (EI, 70 eV, 200 °C) m/z (%) 591 (9) [R_2Bi^+], 435 (100) [$RBiCl^+$], 400 (61) [RBi^+]]. A solution of R_2BiCl (2.7 g, 4.30 mmol) in 30 mL of tetrahydrofuran (THF) was added dropwise at −20 °C to magnesium (0.38 g, 15.7 mmol) activated with 1,2-dibromoethane (0.5 mL). The reaction mixture was stirred for 3 h, and then the temperature was raised to 10 °C. Removal of the solvent in a vacuum, extraction with petroleum ether (80 mL), and filtration and removal of the solvent to dryness give 1.6 g (67%) of dark-red **1** (mp 60 °C). Crystals of **1a**·$CH_3C_6H_5$ and **1b/c**·Et_2O are obtained from solutions of **1** in toluene or diethyl ether at −28 °C: ^{1}H NMR (200 MHz, 25 °C, C_6D_6, TMS) δ 2.06 (12H, s, CH_3), AB spin system with A, 3.47, B, 3.60 (4H, CH_2, $^2J_{HH} =$ 13.6 Hz), 7.20 (2H, d, C_6H_3, $^3J_{HH} = 7.5$ Hz), 7.59 (1H, t, C_6H_3, $^3J_{HH} = 7.5$ Hz); MS (CI_{neg}, NH_3, 200 °C) m/z (%) 1181 (10) [$M^- - H$], 991 (45) [$R_2Bi{-}BiR^-$], 591 (100) [R_2Bi^-], 400 (97) [RBi^-]. Heating a solution of **1** results in a new set of signals: ^{1}H NMR (200 MHz, 75 °C, C_6D_6, TMS) δ 2.04 (12H, s, CH_3), AB spin system with A, 3.29, B, 3.76 (4H, CH_2, $^2J_{HH} = 11.7$ Hz), 7.17 (3H, m, C_6H_3).

Synthesis of [2,6-(Me_2NCH_2)$_2$$C_6H_3$]$_4$$Bi_2$($O_2$) (2). Slow access of air into a solution of **1** in THF or diethyl ether at −28 °C gives the peroxide **2** as a colorless, air-stable crystalline solid (mp 48 °C). Recrystallization from diethyl ether affords single crystals of **2**·Et_2O: MS (CI_{pos}, NH_3, 200 °C) m/z (%) 832 (28) [$R_2Bi_2O_2^+$], 591 (30) [R_2Bi^+], 401 (42) [$RBi^+ + H$], 193 (100) [$R^+ + 2H$].

Synthesis of [2-(Me_2NCH_2)-6-{$Me_2N(O)CH_2$}C_6H_3][2-(Me_2NCH_2)-6-{O(O)C}C_6H_3]Bi (3). Diethyl ether (25 mL) was added slowly to a solution of **1** (0.2 g, 0. 16 mmol) in 15 mL of THF, under argon, and slow diffusion was allowed to take place at room temperature. Slow oxidation, at room temperature, resulted after several weeks in the formation of colorless crystals of **3**: IR (KBr, cm^{-1}) 1602 (COO), 1337 (NO); MS (EI, 70 eV, 200 °C) m/z (%) 577 (70) [$M^+ - O$], 562 (25) [$M^+ - 2O$], 534 (42) [$M^+ - COO - O$], 400 (100) [RBi^+].

Scheme 1



$$4\ 1{,}3\text{-}(Me_2NCH_2)_2C_6H_4 \xrightarrow[-\,4\ BuH]{4\ BuLi} 4\ RLi \xrightarrow[-\,4\ LiCl]{2\ BiCl_3} 2\ R_2BiCl \xrightarrow[-\,MgCl_2]{Mg} \underset{\mathbf{1}}{R_2Bi\text{-}BiR_2}$$

$$R = [2{,}6\text{-}(Me_2NCH_2)_2C_6H_3]$$

X-ray Crystallography. Table 1 lists crystal and refinement data. The data were collected using a Stoe IPDS diffractometer for **1a**·$CH_3C_6H_5$ and a Siemens P4 four-circle diffractometer for **1b/c**·Et_2O, **2**·Et_2O, and **3**, respectively, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The structures were solved by direct methods (full-matrix least squares on F^2). All non-hydrogen atoms were refined with anisotropic thermal parameters. For structure solution and refinement, the software package *SHELX-97* was used.[15] The drawings were created using the *DIAMOND* program by Crystal Impact GbR.[16]

Results and Discussion

The dibismuthane **1** is obtained in a multistep procedure including the arylation of $BiCl_3$ with RLi and the reduction of the resulting diarylbismuth monochloride with magnesium in THF (Scheme 1).

Compound **1** is a dark-red compound, both as a solid and in solutions in hydrocarbons. Single crystals were grown at −28 °C from solutions in toluene or diethyl ether. They contain three different molecular forms of **1**. Monoclinic crystals in the space group $P2_1/c$ consisting of **1a**·$CH_3C_6H_5$ are obtained from toluene. The molecular structure of **1a** is depicted in Figure 1. Crystals obtained from diethyl ether are triclinic (space group $P\bar{1}$). They contain two isomers, **1b** and **1c**, in the asymmetric unit. The structures of **1b** and

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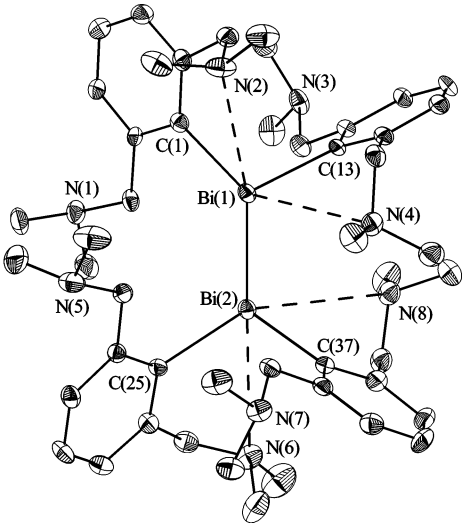

Figure 1. ORTEP-like representation of **1a** in the crystal of **1a**$\cdot CH_3C_6H_5$. The ellipsoids represent a probability of 30%. The hydrogen atoms are omitted for clarity.

1c are shown in Figure 2. Selected interatomic distances and angles are given in Table 2.

In all three forms, the dibismuthane molecules adopt the trans conformation with dihedral angles lp-Bi−Bi-lp of 175.35(3)° (**1a**), 74.80(6)° (**1b**), and 80.37(6)° (**1c**) (lp = assumed position of the lone pair of electrons on the bisector of the obtuse C−Bi−C angle; the dihedral angle was considered to be the angle between these bisectors). The isomers have different types of coordination of the pendant (dimethylamino)methyl arms. In **1a**, four of the pendant Me_2NCH_2 arms, one per aryl group, are bonded through the nitrogen atoms to both bismuth centers, which both display a 3 + 2 coordination pattern with three normal covalent bonds (Bi−Bi, 2 × Bi−C) and two dative bonds from the pendant amino groups [Bi(1)−N(2) 3.241(7) Å, Bi(1)−N(4) 3.236(6) Å and Bi(2)−N(6) 3.284(8) Å, Bi(2)−N(8) 3.335(6) Å; compare the sum of covalent radii, $\sum_{cov}(Bi,N) = 2.22$ Å, and the van der Waals radii, $\sum_{vdw}(Bi,N) = 3.94$ Å, respectively].[14]

In **1b**, 3 + 2 coordination is also achieved for both bismuth atoms; however, the origin of the amino groups is different; i.e., at Bi(3), they originate from different aryl groups [Bi(3)−N(10) 3.241(12) Å and Bi(3)−N(12) 3.183(11) Å] like in **1a**, but at Bi(4), they belong to the same aryl group [Bi(4)−N(15) 3.370(10) Å and Bi(4)−N(16) 3.279(11) Å]. In **1c**, the coordination number at Bi(2) is 3 + 3, with three of the pendant arms involved in coordinative bonding [Bi(2)−N(5) 3.351(9) Å, Bi(2)−N(6) 3.217(11) Å, and Bi(2)−N(7) 3.352(9) Å], whereas at Bi(1), 3 + 2 coordination occurs [Bi(1)−N(1) 3.210(10) Å and Bi(1)−N(4) 3.233(10) Å]. For all three forms of dibismuthane molecules, the N → Bi intramolecular interactions are considerably longer than those observed for the related $R_2Bi{-}BiR_2$ [R = 2-(Me_2NCH_2)-C_6H_4] [Bi−N 2.952(5)−3.170(4) Å].[9] The different environments of the bismuth atoms lead to variations of the Bi−Bi bond lengths [**1a**, 3.0992(6) Å; **1b**, 3.1788(8) Å; **1c**, 3.2092(8) Å]. These values are the longest known Bi−Bi bond lengths in dibismuthanes, and there is little doubt that the elongations result from the increasing coordination by the pendant-arm ligands.

In solution, the different types of coordination of the pendant-arm ligands are not preserved. The ^1H NMR spectrum in C_6D_6 of **1** at +20 °C contains only one set of signals for the 2,6-$(Me_2NCH_2)_2C_6H_3$ groups, i.e., a singlet signal for the methyl groups, an AB spin system for the CH_2 protons, and the signals for the aromatic hydrogen atoms. When the solution is warmed above room temperature, a second set of rather broad 2,6-$(Me_2NCH_2)_2C_6H_3$ signals emerges, with increasing intensities on the cost of the signals of **1**. At +70 °C exclusively, the signals of the high-temperature species are observed. The process is reversible, and on cooling, the signals for **1** appear again. A possible explanation for these findings is to consider the reversible dissociation of **1** with the formation of the diarylbismuth radical $R_2Bi^\bullet$ [R = 2,6-$(Me_2NCH_2)_2C_6H_3$] in solutions of **1**. Dissociative reactions of dibismuthanes have been proposed several times, but even in the case of the sterically encumbered derivative, $R_2Bi{-}BiR_2$ [R = $(Me_3Si)_2CH$], the formation of diorganobismuth radicals was not observed in solution at room temperature.[8,18] By contrast, the dissociation of analogous diphosphanes or diarsanes with the formation of $R_2P^\bullet$ or $R_2As^\bullet$ [R = $(Me_3Si)_2CH$] is a well-established process.[19,20] Dissociation of **1** occurs also under the conditions of electrospray ionization mass spectroscopy (EIMS), and the R_2Bi^+ fragment ion is observed at highest mass. With chemical ionization, however, the molecular ion of **1** can be detected.

Slow access of air to a solution of **1** in THF or diethyl ether at −28 °C gives the peroxide **2**, a colorless, air-stable crystalline solid. Solutions of **2** in organic solvents are unstable at room temperature; they decompose with the elimination of oxygen and the formation of $(R_2Bi)_2O$ [mp 99−103 °C; ^1H NMR (200 MHz, 25 °C, $CDCl_3$, TMS) δ 1.99 (12H, s, CH_3), AB spin system with A, 3.23, B, 3.49 (4H, s, br, CH_2), 7.15 (3H, m, C_6H_3); MS (EI, 70 eV, 200 °C) *m*/*z* (%) 1007 (1) [$R_2BiOBiR^+$], 816 (1) [R_2BiOBi^+], 591 (100) [R_2Bi^+], 417 (80) [$RBiOH^+$], 400 (77) [RBi^+]; the same compound was isolated from hydrolysis of the monochloride R_2BiCl]. A reaction path leading to **2** is given in Scheme 2.

Compound **2** crystallizes from diethyl ether as **2**$\cdot Et_2O$ in the space group $P\bar{1}$. The structure was determined by X-ray diffraction. Selected interatomic distances and angles are given in Table 3. The molecules of **2** consist of two R_2Bi units bridged by an O_2 group, which adopts a position intermediate between the end-on and side-on bridging coordination (Figure 3). The O−O bond length [1.515(7) Å] in **2** corresponds to a single bond and is only slightly

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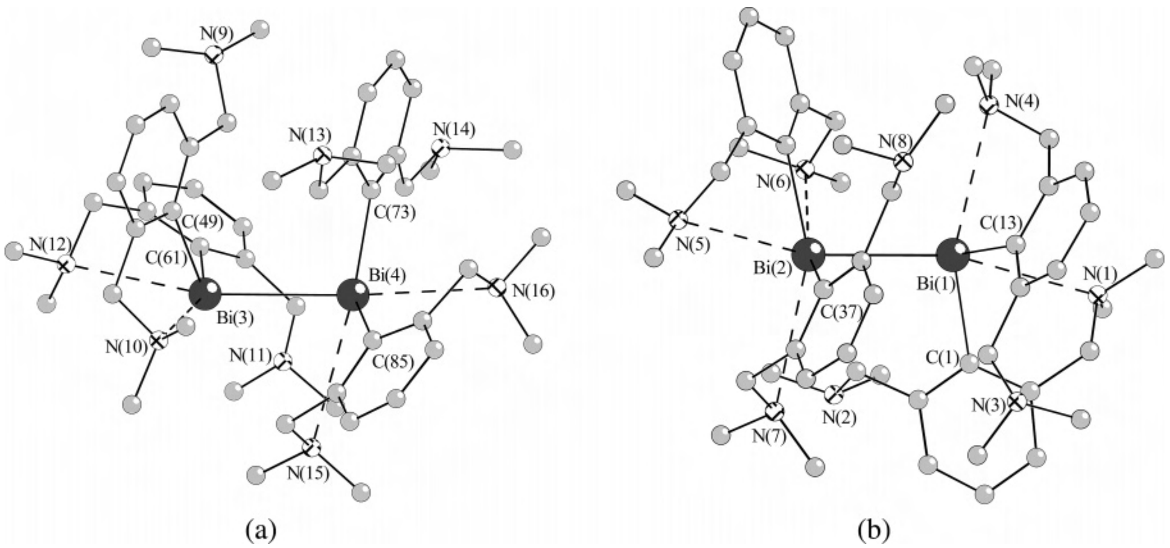

Figure 2. Structures of (a) **1b** and (b) **1c** in the crystal of **1b/c**·Et_2O. The hydrogen atoms are omitted for clarity.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **1**

	Molecule **1a**		
Bi(1)−Bi(2)	3.0992(6)	C(1)−Bi(1)−C(13)	94.5(2)
Bi(1)−C(1)	2.324(7)	C(1)−Bi(1)−Bi(2)	104.38(17)
Bi(1)−C(13)	2.303(6)	C(13)−Bi(1)−Bi(2)	97.10(17)
Bi(2)−C(25)	2.376(7)	C(25)−Bi(2)−C(37)	99.0(2)
Bi(2)−C(37)	2.300(7)	C(25)−Bi(2)−Bi(1)	103.29(17)
Bi(1)−N(2)	3.241(7)	C(37)−Bi(2)−Bi(1)	97.80(18)
Bi(1)−N(4)	3.236(6)		
Bi(2)−N(6)	3.284(8)		
Bi(2)−N(8)	3.335(6)		
	Molecule **1b**		
Bi(3)−Bi(4)	3.1788(8)	C(49)−Bi(3)−C(61)	100.0(4)
Bi(3)−C(49)	2.323(11)	C(49)−Bi(3)−Bi(4)	101.5(3)
Bi(3)−C(61)	2.331(10)	C(61)−Bi(3)−Bi(4)	100.6(3)
Bi(4)−C(73)	2.332(11)	C(73)−Bi(4)−C(85)	101.6(4)
Bi(4)−C(85)	2.306(11)	C(73)−Bi(4)−Bi(3)	100.3(3)
Bi(3)−N(10)	3.241(12)	C(85)−Bi(4)−Bi(3)	108.3(3)
Bi(3)−N(12)	3.183(112)		
Bi(4)−N(15)	3.370(10)		
Bi(4)−N(16)	3.279(11)		
	Molecule **1c**		
Bi(1)−Bi(2)	3.2092(8)	C(1)−Bi(1)−C(13)	100.2(4)
Bi(1)−C(1)	2.321(11)	C(1)−Bi(1)−Bi(2)	102.6(3)
Bi(1)−C(13)	2.297(10)	C(13)−Bi(1)−Bi(2)	103.0(3)
Bi(2)−C(25)	2.327(11)	C(25)−Bi(2)−C(37)	101.4(4)
Bi(2)−C(37)	2.338(10)	C(25)−Bi(2)−Bi(1)	103.9(3)
Bi(1)−N(1)	3.210(10)	C(37)−Bi(2)−Bi(1)	102.1(2)
Bi(1)−N(4)	3.233(10)		
Bi(2)−N(5)	3.351(9)		
Bi(2)−N(6)	3.217(11)		
Bi(2)−N(7)	3.352(9)		

Scheme 2

$$\underset{\mathbf{1}}{R_2Bi\text{-}BiR_2} \rightleftharpoons 2\,R_2Bi\bullet \xrightarrow{O_2} \underset{\mathbf{2}}{R_2Bi\text{-}O\text{-}O\text{-}BiR_2}$$

$R = [2,6\text{-}(Me_2NCH_2)_2C_6H_3]$

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for **2**

Bi(1)−O(1)	2.138(5)	C(1)−Bi(1)−C(13)	101.3(2)
Bi(1)−C(1)	2.285(6)	O(1)−Bi(1)−C(1)	92.0(2)
Bi(1)−C(13)	2.292(6)	O(1)−Bi(1)−C(13)	88.0(2)
Bi(1)−N(1)	3.148(7)	C(25)−Bi(2)−C(37)	98.2(2)
Bi(1)−N(2)	2.873(6)	O(2)−Bi(2)−C(25)	98.2(2)
Bi(2)−O(2)	2.171(5)	O(2)−Bi(2)−C(37)	87.1(2)
Bi(2)−C(25)	2.275(6)	O(1)−Bi(2)−O(2)	33.93(16)
Bi(2)−C(37)	2.305(7)	O(1)−Bi(2)−C(25)	132.10(19)
Bi(2)−N(5)	3.083(9)	O(1)−Bi(2)−C(37)	81.97(19)
Bi(2)−N(6)	2.848(5)	O(2)−O(1)−Bi(1)	99.5(3)
Bi(1)−O(2)	2.817 (5)	O(2)−O(1)−Bi(2)	53.1(2)
Bi(2)−O(1)	2.710(5)	Bi(1)−O(1)−Bi(2)	149.6(2)
O(1)−O(2)	1.515(7)	O(1)−O(2)−Bi(2)	93.0(3)

longer than the corresponding distances in H_2O_2 (1.475 Å) or the peroxo cluster $(Ph_2SbO)_4(O_2)_2$ [1.461(4) and 1.466(5) Å].[21] Also, the Bi(1)−O(1) [2.138(5) Å] and Bi(2)−O(2) [2.171(5) Å] distances are consistent with single bonds; they are, however, longer than those found for $(Mes_2Bi)_2O$ [Bi−O 2.075(8) and 2.064(7) Å].[6] The distances Bi(1)−O(2) [2.817(5) Å] or Bi(2)−O(1) [2.710(5) Å] lie between the values for single bonds and van der Waals contact distances of the Bi and O atoms [compare the sum of covalent radii, $\sum_{cov}(Bi,O) = 2.16$ Å, and the van der Waals radii, $\sum_{vdw}(Bi,O) = 3.80$ Å, respectively].[17] The Bi(1)−O(1)−O(2) and O(1)−O(2)−Bi(2) bond angles in **2** are 99.5(3) and 93.0(3)°, respectively. The Bi_2O_2 unit is folded [dihedral angles Bi(1)−O(1)−Bi(2)/Bi(1)−O(2)−Bi(2) 44.1(6)° and O(1)−Bi(1)−O(2)/O(1)−Bi(2)−O(2) 14.6(2)°], with wide Bi−O−Bi [149.6(2) and 139.3(1)°] and acute O−Bi−O [32.05(15) and 33.93(16)°] angles. The bonding of the peroxo bridge can be described as a combination of normal covalent Bi(2)−O(2) and Bi(1)−O(1) and dative O(1) → Bi(2) and O(2) → Bi(1) bonds. The C_2BiO core at a metal center is pyramidal with the bond angles at the Bi atoms [range 87.1(2)−101.3(2)°] generally more acute than in those in **1a** [range 94.5(2)−104.38(17)°]. For each metal center, two intramolecular N−Bi interactions are established by nitrogen atoms of the same aryl group; the shorter ones are trans to an oxygen atom [Bi(1)−N(2) 2.873(6) Å, N(2)−Bi(1)−O(1) 153.7(1)° and Bi(2)−N(6) 2.848(5) Å, N(6)−Bi(2)−O(2) 159.9(1)°], while the longer ones are trans to a carbon atom [Bi(1)−N(1) 3.148(7) Å, N(1)−Bi(1)−C(13) 153.1(2)° and Bi(2)−N(5) 3.083(9) Å, N(5)−Bi(2)−C(37) 147.0(2)°; a weaker interaction involving the disordered N(3) atom, Bi(1)−N(3B) 3.41(4) Å, can also be considered]. Almost orthogonal to the Bi_2O_2 core lie the Bi−C bonds of the other

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[21] Breunig, H. J.; Krüger, T.; Lork, E. *J. Organomet. Chem.* **2002**, *648*, 209.

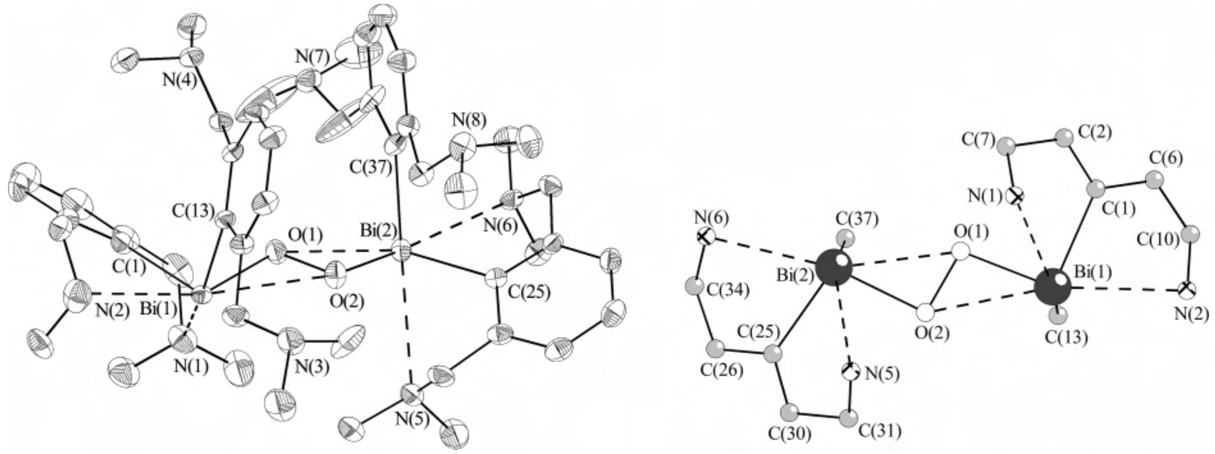
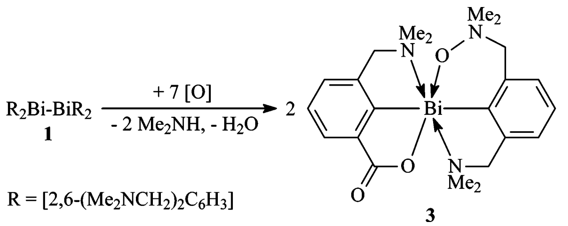


Figure 3. (a) ORTEP-like representation at 40% probability of **2** in the crystal of **2**·Et_2O (the hydrogen atoms are omitted for clarity). (b) Environment around the Bi atoms in **2**.

Scheme 3



pair of aryl substituents, where the amino groups are directed away from the bismuth atoms. If the additional longer Bi−O contacts are not considered, the coordination about the metal centers is again tetragonal pyramidal [C(1) and C(25) atoms in apical positions, respectively], with a higher degree of distortion than that in **1a**.

When a THF/Et_2O solution of the dibismuthane **1** is exposed to air at room temperature, the oxidation proceeds with cleavage of the Bi−Bi bond and formation of the mononuclear diarylbismuth carboxylate **3**. In the course of the reaction, one of the pendant (dimethylamino)methyl groups is transformed into an amine oxide and another one is oxidized to a carboxyl group, which is intramolecularly bonded to the bismuth center. An equation describing the formation of **3** is proposed in Scheme 3. The side products were not identified. A similar conversion to an amine oxide derivative, i.e., $Me_2(O)N(CH_2)_3Sn(OCOCH_2)_3N$, was observed during the reaction of the oxidation of $Me_2N(CH_2)_3$-$SnPh_3$ with $N(CH_2COOH)_3$ in dimethylformamide.[22]

It is very likely that the peroxide **2** is involved in the oxidation process as a source of the oxygen atoms. Peroxides are powerful oxidation agents that are also used for the transformation of amines to amine oxides. Crystals of **3** belong to the monoclinic space group $P2_1/c$. They consist of molecules containing bismuth bonded to a (C,O)-bidentate chelating aryl carboxylato ligand derived from 3-[(dimethylamino)methyl]benzoic acid and a second aryl group (Figure 4). Selected interatomic distances and angles are given in Table 4.

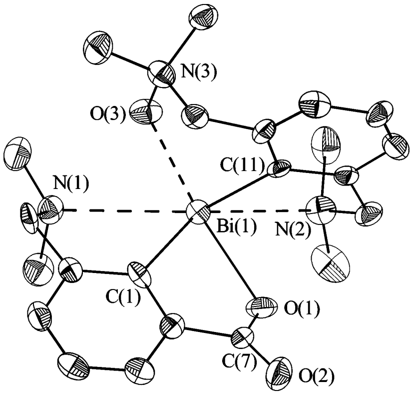


Figure 4. ORTEP-like representation at 50% probability of **3**. The hydrogen atoms are omitted for clarity.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for **3**

Bi(1)−C(1)	2.274(8)	C(1)−Bi(1)−C(11)	102.9(3)
Bi(1)−C(11)	2.270(8)	C(1)−Bi(1)−O(1)	70.8(3)
Bi(1)−O(1)	2.395(6)	C(11)−Bi(1)−O(1)	77.5(2)
Bi(1)−O(3)	2.372(7)	C(1)−Bi(1)−O(3)	94.2(3)
Bi(1)−N(1)	3.019(8)	C(11)−Bi(1)−O(3)	80.6(3)
Bi(1)−N(2)	2.834(9)	O(1)−Bi(1)−O(3)	149.7(2)
O(1)−C(7)	1.295(10)	N(3)−O(3)−Bi(1)	125.3(5)
O(2)−C(7)	1.253(10)	O(3)−N(3)−C(20)	110.8(7)
O(3)−N(3)	1.404(9)	O(3)−N(3)−C(21)	108.2(7)
		O(3)−N(3)−C(22)	109.8(7)
		C(20)−N(3)−C(21)	108.6(8)
		C(20)−N(3)−C(22)	111.3(7)
		C(21)−N(3)−C(22)	108.1(8)

Because of the formation of the five-membered BiC_3O ring, the pyramidal geometry of the C_2BiO core is irregular, with two O−Bi−C angles considerably smaller than 90° [O(1)−Bi(1)−C(1) 70.8(3)° and O(1)−Bi(1)−C(11) 77.5(2)°] and a C(1)−Bi(1)−C(11) angle of 102.9(3)°. The Bi−C bond lengths [Bi(1)−C(1) 2.274(8) Å and Bi(1)−C(11) 2.270(8) Å] are comparable with the corresponding bonds found in **1** or **2**. The O(3) atom of the amine oxide pendant arm is coordinated to the metal center, thus resulting in a six-membered BiC_3NO ring. The Bi−O bond lengths [Bi(1)−O(1) 2.395(6) Å and Bi(1)−O(3) 2.372(7) Å] are longer than the values observed for the Bi−O single bond in $(Mes_2Bi)_2O$ [Bi−O 2.095(18) and 2.117(19) Å[5] and 2.075(8) and 2.064(7) Å[6]]. Similar values were observed for diphenylbismuth *N*-benzoylglycinate, a polymeric diorganobismuth(III) carboxylate with bridging carboxylato groups [Bi−O

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(22) Dakternieks, D.; Dyson, G.; Jurkschat, K.; Tozer, R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1993**, *458*, 29.

2.396(6) and 2.484(6) Å],[23] or for the closely related hypervalent mononuclear bismuth(III) species [2,6-($Me_2NCH_2)_2C_6H_3$]Bi[$C_6H_4\{C(CF_3)_2O\}$-2] [Bi−O 2.194(9) Å].[14]

The inner-coordination sphere around the bismuth center of **3** can be described as distorted *pseudo* trigonal bipyramidal, with C(1) and C(11) in equatorial positions and O(1) and O(2) in axial positions [O(1)−Bi(1)−O(3) 149.7(2)°]. Additional trans intramolecular Bi−N interactions [Bi(1)−N(1) 3.019(8) and Bi(1)−N(2) 2.834(9) Å; N(1)−Bi(1)−N(2) 142.1(2)°] are established by the two remaining Me_2NCH_2 pendant arms, resulting in five-membered BiC_3N rings. When also the amino groups are considered, a distorted octahedral coordination results.

Conclusions

The formation of a new tetraaryldibismuthane with protection by eight pendant-arm amino ligands, which exist in different crystalline forms with remarkably long Bi−Bi bond lengths, and a tendency to insert dioxygen from air probably via the intermediate formation of diorganobismuth radicals open interesting perspectives for applications of the dibismuthane oxygen system as a strong oxidant, which at room temperature performs the transformation of a (dimethylamino)methyl group into a carboxyl group.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[23] Huber, F.; Domagala, M.; Preut, H. *Acta Crystallogr.* **1988**, *C44*, 828.