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Synthesis and Structure of Monoorganobismuth Compounds Bearing Pyridinedimethoxide Ligands

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Monoorganobismuth compounds bearing pyridinedimethoxide ligands $[2,6\text{-}C_5H_3N(CR^1{}_2O)_2]^{2-}$ (R^1 = Me, Et, ^{i}Pr) have been synthesized. The ligand exchange reaction of $PhBi(OEt)_2$, which was in situ generated from $PhBiBr_2$ and 2 equiv of NaOEt, with $[2,6\text{-}C_5H_3N(CR^1{}_2OH)_2]$ (**1a**, R^1 = Me; **1b**, R^1 = Et; **1c**, R^1 = ^{i}Pr) gave $PhBi[2,6\text{-}C_5H_3N(CR^1{}_2O)_2]$ (**5a**, R^1 = Me; **5b**, R^1 = Et; **5c**, R^1 = ^{i}Pr) in 57−78% yields. A similar reaction of $MeBi(OEt)_2$ with **1a** gave $MeBi[2,6\text{-}C_5H_3N(CMe_2O)_2]$ (**5d**) in 96% yield. $(EtO)Bi[2,6\text{-}C_5H_3N(CEt_2O)_2]$ (**5e**) was also synthesized by the reaction of $Bi(OEt)_3$ with **1b** in 61% yield. The structures of **5a**−**5c** and **5e** were characterized by X-ray structure analysis. Compounds **5a**−**5c** and **5e** form dimers in the solid state through the intermolecular coordination of the oxygen atoms to the bismuth atoms. The intermolecular Bi−O distances highly depend on the bulkiness of R^1 groups and range from 2.699(2) Å (**5a**) to 3.581(3) Å (**5c**). In solution at room temperature, on the other hand, **5a**−**5e** exist as monomers judging from NMR spectra in $CDCl_3$ and/or toluene-d_8.

Introduction

Since bismuth generally is believed to be a nontoxic element,[1] we have become interested in organic synthesis using organobismuth reagents.[2] However, their application to organic synthesis is still limited.[1,3] Most organobismuth(III) reagents so far used in organic synthesis are triaryl- and trialkylbismuth compounds. The presence of three reactive Bi−C bonds in a molecule makes their chemistry complicated, and a mechanistic study is not straightforward. In this context monoorganobismuth dialkoxides appear to be suitable compounds for the investigation on the reactivity of a Bi−C bond. However, a survey of the literature reveals that most of monoorganobismuth dialkoxides so far reported have very low solubility in common organic solvents presumably because of the formation of oligomeric or polymeric structures due to the strong intermolecular Bi−O interactions.[4] Furthermore, these compounds are moisture-sensitive, and some of them are thermally unstable. To obtain monoorganobismuth dialkoxides possessing improved solubility and stability, we have designed alkoxide ligands $[2,6\text{-}C_5H_3N(CR^1{}_2O)_2]^{2-}$. These ligands, similar to those used by Lee and Martin,[5] allow introduction of substituent R^1 in the proximity of the oxygen atoms, which enhances the solubility. In addition, intramolecular coordination of the nitrogen atom to the bismuth atom may serve to weaken the intermolecular coordination between oxygen and bismuth atoms. Here we report the synthesis and the structure of $R^2Bi[2,6\text{-}C_5H_3N(CR^1{}_2O)_2]$ (R^1 = Me, Et, ^{i}Pr; R^2 = Ph, Me, OEt).

Results and Discussion

Synthesis. Pyridinedimethanols $[2,6\text{-}C_5H_3N(CR^1{}_2OH)_2]$ **1a**−**1c** were synthesized by the reaction of $2,6\text{-}C_5H_3N(CO_2Me)_2$ with an excess of Grignard reagent as described in the literature (Scheme 1).[6] Methyl (**1a**) and ethyl (**1b**) derivatives were obtained in satisfactory yields, while the bulkier isopropyl compound (**1c**) was obtained only in 19% yield. An initial attempt to synthesize **5a** by the sequence of lithiation of **1a** with 2 equiv of n-BuLi and the subsequent reaction with $PhBiBr_2$ failed. An alternative procedure involving the conversion of $PhBiBr_2$ to $PhBi(OEt)_2$ (**2**)[4a] by 2 equiv of NaOEt and the subsequent ligand exchange reaction between **2** and **1a** successfully afforded desired compound **5a** in 78% yield (Scheme 2). Compounds **5b** and **5c** were similarly prepared in 57% and 62% yields, respectively. Similar procedures gave methyl derivative **5d** in 96% yield from **1a** and $MeBi(OEt)_2$ (**3**)[4c] and ethoxy compound **5e** in 61% yield from **1b** and $Bi(OEt)_3$ (**4**).[7] Starting **3** or **4** was generated in situ from $MeBiCl_2$ or $BiCl_3$, respectively, with NaOEt (2 equiv for $MeBiCl_2$

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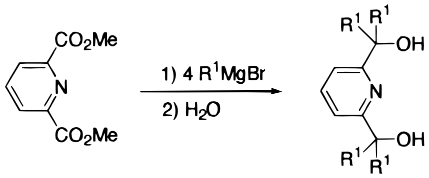
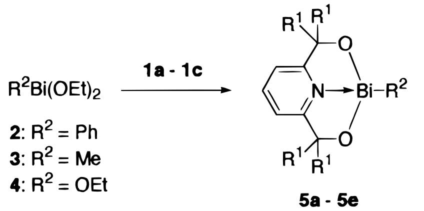
Scheme 1



1a: R^1 = Me
1b: R^1 = Et
1c: R^1 = ^{i}Pr

Scheme 2



2: R^2 = Ph
3: R^2 = Me
4: R^2 = OEt

5a - 5e

5a: R^1 = Me, R^2 = Ph
5b: R^1 = Et, R^2 = Ph
5c: R^1 = ^{i}Pr, R^2 = Ph
5d: R^1 = R^2 = Me
5e: R^1 = Et, R^2 = OEt

and 3 equiv for $BiCl_3$). Compounds **5a**−**5e** are soluble in common organic solvents such as toluene, THF, and CH_2Cl_2. As expected, the solubility increases in the order **5a** < **5b** < **5c**. Organobismuth compounds **5a**−**5d** are stable at least for several days to air in the solid state, while they hydrolyze in solution upon exposure to air. Ethoxy compound **5e** hydrolyzes even in the solid state upon exposure to air for a few hours.

Crystal and Molecular Structures. The crystal structures of **5a**−**5c** and **5e** were determined by X-ray structure analysis. Crystallographic data are summarized in Table 1. Selected bond distances and angles are listed in Table 2. In case of **5a**, needle-type crystals containing THF molecules were easily obtained by the recrystallization from THF, although the quality was not good enough for X-ray analysis. Fortunately, X-ray-quality crystals of **5a** were obtained from an NMR sample in C_6D_6. Interestingly, the crystals contained one molecule of H_2O per every two molecules of **5a**. The H_2O molecule is presumed to have come from the solvent. In the asymmetric unit of **5a**, two independent molecules exist, both of which form dimers in the solid state through the Bi−O intermolecular coordination. The molecular structure of one of the dimers is shown in Figure 1. The geometry at the bismuth atom can be described as highly distorted square pyramid, in which a stereoactive lone pair of electrons probably occupies the vacant position trans to the phenyl group. A very similar arrangement has been reported for bis(1-oxopyridine-2-thiolato)phenylbismuth,[8] although it is a monomeric compound. The intramolecular Bi−O distances (2.21−2.30 Å) and the Bi−C distances (2.26−2.27 Å) are comparable to those found in the literatures.[9,10] The Bi−N distances (2.34−2.35 Å) are longer than the known Bi−N single bond (2.12−2.28 Å),[11] but shorter than those reported for the bismuth compounds bearing pentadentate pyridine ligands (2.44−2.47 Å).[12,13] The intermolecular Bi−O distances, 2.699(3) and 2.761(3) Å, are much longer than the intramolecular ones and are in the range observed for coordinative Bi−O distances.[14] The pyridine ring and Bi1, O1, O2, C2, C3 atoms are almost coplanar, and the maximum deviation (for O2) from the least-squares plane is 0.061(4) Å. As shown in the crystal packing diagram of **5a** (Figure 2), only one of the two independent dimers is connected to two H_2O molecules through hydrogen bonds, forming an indefinite chain along the *a* axis. The other dimer does not have any interaction with H_2O while it also forms an independent column in the crystal.

As shown in Figures 3 and 4, **5b** and **5c** also form dimers in the solid state. Compound **5b** crystallizes in the *C*2/*c* space group, and the two apical phenyl groups in the dimer point to the same side (syn), while **5c** crystallizes in the $P\bar{1}$ space group and the two apical phenyl groups are directed to the opposite side (anti), as observed for **5a**. The intramolecular Bi−O, Bi−N, and Bi−C distances of **5b** and **5c** are similar to those of **5a**. On the other hand, the intermolecular Bi−O distances highly depend on the bulkiness of the substituent R^1 and are 2.907(5) Å for **5b** and 3.581(3) Å for **5c**. Although, the distance for **5c** is close to the sum of the van der Waals radii (3.67 Å),[15] the intermolecular Bi−O interaction seems to still exist in **5c** judging from its crystal structure. The N1−Bi1−C1 angles also depend of the bulkiness of the substituent R^1 and range from 93.3(2)° (**5a**) to 105.4(1)° (**5c**). The planarities of Bi-containing fused rings also decrease in **5b** and **5c**. The maximum deviations from the least-squares plane are 0.176(5) Å (O1) for **5b** and 0.314(6) Å (one of the carbon atoms in the pyridine ring) for **5c**.

As Figure 5 shows, **5e** has a dimeric structure similar to that of **5a**. The EtO group occupies the apical position, and its oxygen atom does not have intermolecular

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Table 1. Summary of Crystal Data for Compounds 5a, 5b, 5c, and 5e

	5a	**5b**	**5c**	**5e**
formula	$C_{17}H_{20}BiNO_2 \cdot 1/2H_2O$	$C_{21}H_{28}BiNO_2$	$C_{25}H_{35}BiNO_2 \cdot CH_2Cl_2$	$C_{17}H_{28}BiNO_3$
fw	488.34	535.44	675.47	503.39
cryst size, mm	0.25 × 0.12 × 0.20	0.12 × 0.10 × 0.23	0.25 × 0.25 × 0.20	0.15 × 0.15 × 0.10
a, Å	10.859(1)	22.304(3)	10.726(3)	10.068(3)
b, Å	15.024(2)	11.130(4)	13.653(1)	11.882(3)
c, Å	10.5933(9)	16.807(3)	10.643(2)	8.346(3)
α, deg	94.287(8)		90.98(1)	93.32(3)
β, deg	91.922(8)	94.07(1)	119.28(2)	111.14(2)
γ, deg	88.003(9)		83.13(1)	91.49(2)
V, Å^3	1651.7(9)	4161(1)	1348.2(6)	928.5(5)
cryst syst	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Z	4	8	2	2
D_{calc}, g cm^{-3}	1.88	1.71	1.66	1.80
$F(000)$	932.00	2080.00	666.00	488.00
μ (Mo Kα), cm^{-1}	102.30	84.70	67.47	94.89
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
T, K	296	223	203	193
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
$2\theta_{max}$, deg	55.0	55.0	54.9	55.2
no. of rflns measd	8164	4946	6465	4488
no. of unique rflns	7862 ($R_{int} = 0.016$)	4779 ($R_{int} = 0.022$)	6136 ($R_{int} = 0.031$)	4242 ($R_{int} = 0.050$)
no. of rflns used, $I_o > 3.0\sigma(I_o)$	6243	3277	5599	3127
no. of variables	389	222	290	199
R, R_w	0.026, 0.033	0.030, 0.039	0.029, 0.039	0.041, 0.049
GOF	1.30	1.04	1.41	1.32
diff peak, hole, e Å^{-3}	0.83, −1.38	0.61, −0.67	1.16, −2.10	0.90, −2.60

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5a, 5b, 5c, and 5e

	5a	**5b**	**5c**	**5e**
Bi1−O1	2.215(3), 2.212(3)	2.223(4)	2.201(3)	2.184(6)
Bi1−O2	2.230(3), 2.297(3)	2.243(4)	2.189(3)	2.223(6)
Bi1−O3				2.099(8)
Bi1−O1*	2.761(3), 2.699(3)	2.907(5)	3.581(3)	2.709(5)
Bi1−N1	2.349(4), 2.338(4)	2.317(5)	2.330(3)	2.334(7)
Bi1−C1	2.261(5), 2.269(5)	2.240(7)	2.263(4)	
O1−Bi1−O2	140.3(1), 139.9(1)	140.4(2)	138.6(1)	139.9(2)
O1−Bi1−O3				86.1(3)
O1−Bi1−O1*	71.8(1), 69.6(1)	70.4(2)	92.79(9)	68.4(2)
O1−Bi1−N1	70.3(1), 70.6(1)	70.9(2)	70.4(1)	70.5(2)
O1−Bi1−C1	89.8(2), 90.9(2)	90.9(2)	88.9(1)	
O2−Bi1−O3				94.0(3)
O2−Bi1−O1*	147.8(1), 150.5(1)	149.0(1)	128.36(8)	151.6(2)
O2−Bi1−N1	70.1(1), 69.3(1)	70.4(2)	70.5(1)	69.4(2)
O2−Bi1−C1	90.3(2), 90.0(2)	88.4(2)	88.8(1)	
O3−Bi1−N1				93.0(3)
N1−Bi1−C1	93.3(2), 93.3(2)	100.9(2)	105.4(1)	

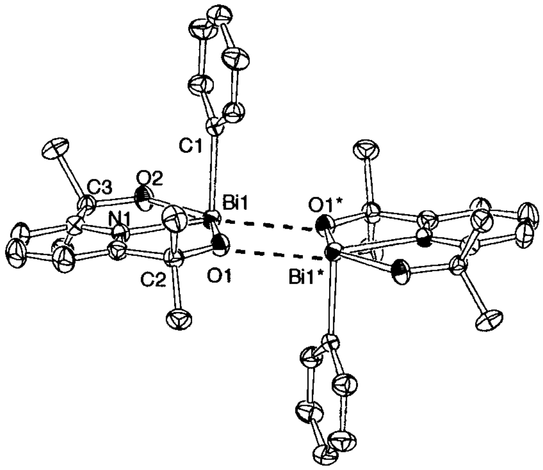

Figure 1. Molecular structure of the dimeric pair of **5a** (30% probability).

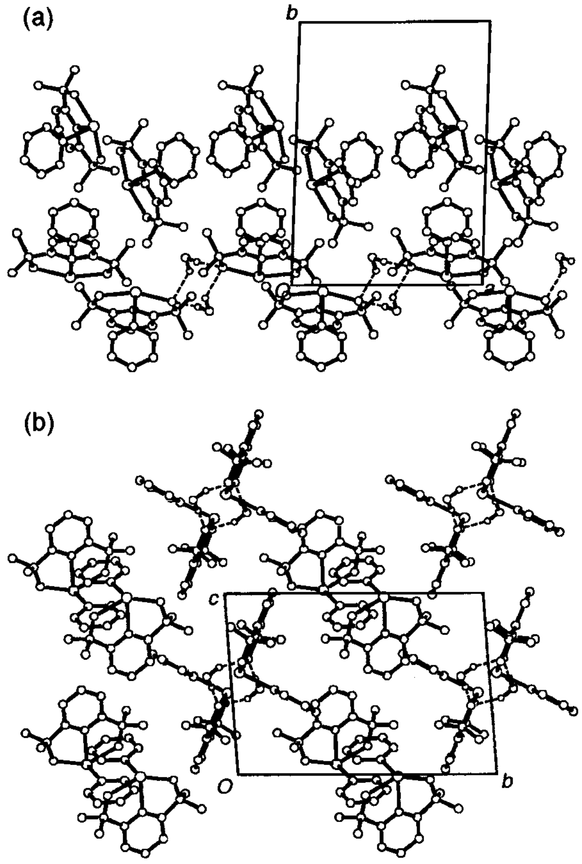

Figure 2. Crystal packing of **5a** (a) along the *c* direction and (b) along the *a* direction. Dashed lines indicate hydrogen bonds.

interaction with the bismuth atom. The intermolecular Bi−O distance of **5e** (2.709(5) Å) is almost the same as that of **5a**. Similarly to **5a**, pyridine rings and Bi1, O1, O2, N1, C2, C3 atoms of **5e** are almost coplanar. The maximum deviation from the least-squares plane is 0.05(1) Å (C3). The apical Bi1−O3 distance (2.099(8) Å) is much shorter than the Bi1−O1 and Bi1−O2 distances, as observed in other square pyramidal bismuth compounds.[9a,12b,16]

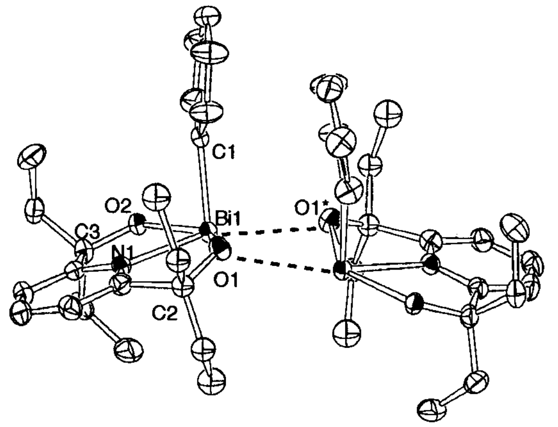

Figure 3. Molecular structure of the dimeric pair of **5b** (30% probability).

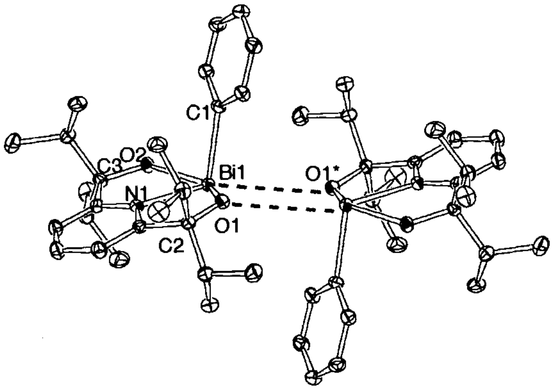

Figure 4. Molecular structure of the dimeric pair of **5c** (30% probability).

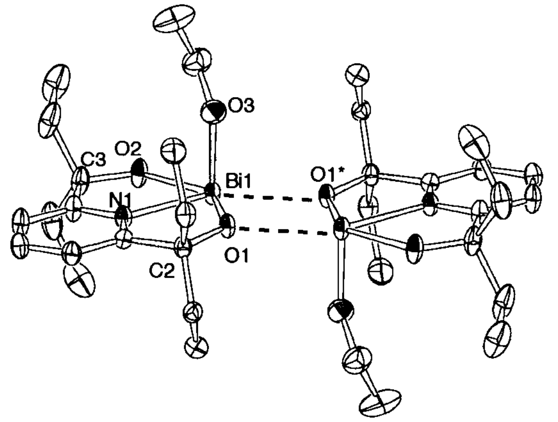

Figure 5. Molecular structure of the dimeric pair of **5e** (30% probability).

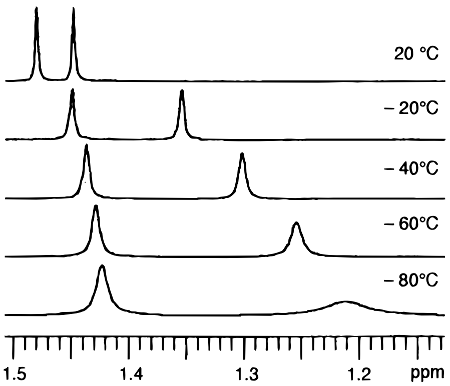

Figure 6. Methyl proton signals in the VT-^{1}H NMR spectra of **5a** in CD_2Cl_2.

Table 3. ^{1}H NMR Chemical Shifts of Phenyl Protons of 5a–5c, Ph_3Bi, and Some Other Phenylbismuth Compounds in $CDCl_3$

compound	*o*-H/ppm	*m*-H/ppm	*p*-H/ppm
5a	8.59	7.62	7.20
5b	8.50	7.64	7.20
5c	8.56	7.69	7.21
Ph_3Bi	7.79	7.43	7.36
PhBi(OCOCH=CHCOO)^{a,b}	8.53–8.76	7.66–7.98	7.21–7.44
$PhBiCl_2$^{c,d}	8.99	7.96	7.43
$PhBiBr_2$^{c,d}	9.14	7.94	7.44
$PhBi(SCH_2CH_2S)$^{e}	8.15	7.60	7.32

[a] Phenylbismuth maleate, ref 13. [b] In DMSO-d_6. [c] Reference 14. [d] In acetone-d_6. [e] Reference 4b. The values shown here were obtained by ourselves.

NMR Spectra. ^{1}H and ^{13}C NMR spectra of **5a**–**5e** in $CDCl_3$ at room temperature displayed only the signals assignable for the monomeric species, suggesting that the integrity of the dimeric structures is not retained in solution. Variable-temperature ^{1}H NMR study of **5a** in CD_2Cl_2 or toluene-d_8 did not show any new signal even at −80 °C. However, as shown in Figure 6, the higher field signal arising from one of the two methyl groups of **5a** in CD_2Cl_2 largely upfield shifted and broadened by lowering the temperature. The difference between the chemical shift value due to this methyl group at 20 °C and the value at −80 °C was −0.24 ppm (the minus sign in the chemical shift difference means upfield shift). On the other hand, the corresponding difference between the values due to the other methyl group was only −0.06 ppm. The chemical shifts of the phenyl proton signals were also temperature dependent, the differences between the values at 20 °C and at −80 °C being 0.19, −0.03, and −0.03 ppm for *o*-, *m*-, and *p*-protons, respectively. The differences for the pyridine protons, which behaved similarly, were respectively 0.12 and 0.07 ppm for 3- and 4-protons. Larger chemical shift differences were observed for the protons nearer to the bismuth center. This presumably suggests that although a rapid monomer–dimer interchange occurs even at −80 °C, the relative concentration of the dimer increases with lowering of the temperature.

Table 3 shows the ^{1}H NMR chemical shifts of phenyl protons of **5a**–**5c** along with those of relevant phenyl bismuth compounds. The signals of the ortho protons of **5a**–**5c** are considerably downfield shifted, as compared with that of Ph_3Bi. The meta protons of **5a**–**5c** also show downfield shifts to smaller extents, while the signals for the para protons are slightly upfield shifted. Other phenylbismuth dicarboxylate,[17] dihalide,[18] and dithiolate[4b] also show similar downfield shifts for ortho and meta protons. Table 4 summarizes the ^{13}C NMR chemical shifts of the bismuth-bound carbons with

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Table 4. ^{13}C NMR Chemical Shifts of the Carbons Directly Attached to Bismuth Atoms in CDCl$_3$

compound	chemical shift/ppm	Δδ/ppm[b]
Ph_3Bi	155.26	
5a	206.97	51.71
5b	208.85	53.59
5c	210.43	55.17
Me_3Bi	−6.71	
5d	63.89	70.60
$(Me_3Si)_2CHBiCl_2$[a]	69.69	

[a] In C_6D_6. [b] The difference in chemical shift between **5a**−**5c** and Ph_3Bi or **5d** and Me_3Bi.

reference to the relevant data for Ph_3Bi or Me_3Bi. For **5a**−**5c**, large downfield shifts were observed as compared with Ph_3Bi. Compound **5d** also showed large downfield shifts relative to Me_3Bi. Since the ^{13}C NMR signals of bismuth-bound carbons are extremely weak or not observed due to the adjacent bismuth atoms, their chemical shift data are sorely lacking in the literature. However, our observations for **5a**−**5d** are in agreement with a recent paper reporting an alkylbismuth dichloride, $(Me_3Si)_2CHBiCl_2$, which also shows a considerable downfield shifts for the *C*Bi signal.[19]

Conclusion

Monoorganobismuth compounds bearing 2,6-pyridinedimethoxide ligands are easily prepared in moderate to excellent yields by the ligand exchange reaction of phenylbismuth diethoxide or methylbismuth diethoxide with corresponding pyridinedimethanols **1a**−**1c**. These compounds form dimers through the intermolecular oxygen coordination to bismuth in the solid state. Each unit in the dimeric form adopts a distorted square pyramidal configuration with the organic ligand placed at the apical positions. The intermolecular Bi−O distances very much depended on the bulkiness of the pyridinedimethoxy ligands. Compounds **5a**−**5d** are soluble in common organic solvents, but the dimeric structures do not persist in solution. The compounds will be useful to investigate the reactivity of the Bi−C bond and related synthetic reactions.

Experimental Section

General Procedures. All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk tube techniques. Toluene was distilled from Na/benzophenone ketyl. All other anhydrous solvents were purchased from Kanto Chemicals or Aldrich and were used as received. Compound **1a**,[6] $PhBiBr_2$,[18,20] and $MeBiCl_2$[21] were prepared according to literature procedures. $BiCl_3$ was purchased from Kojundo Chemical Laboratory and used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ARX300 and JEOL LA500 spectrometers. Chemical shifts are given in ppm and are referenced to tetramethylsilane. Coupling constants are reported in hertz.

2,6-Pyridinebis(diethylmethanol) (1b). The procedure reported by Lukes and Pergál was slightly modified as follows.[6] To a mixture of 210 mL of an ether solution of ethylmagnesium chloride (3.0 M, 0.63 mol) and 300 mL of toluene was added 27.0 g of dimethyl 2,6-pyridinedicarboxylate (0.138 mol) in 5 portions over a period of 20 min with ice-cooling. The resulting wine red suspension was gradually heated to 105 °C (2.5 h) with concurrent removal of ether. After cooling, water (400 mL) was carefully added to the mixture with ice-cooling, and then 300 mL of EtOAc was added. The mixture was filtered through Celite under reduced pressure, and the remaining solid was washed with EtOAc (6 × 100 mL). The filtrate was separated, and the organic layer was washed with water (2 × 100 mL). The aqueous layer was extracted with EtOAc (2 × 100 mL), and the extract was washed with water (2 × 80 mL). The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated in vacuo. The crude mixture was purified by chromatography on silica gel (hexane/^{i}PrOH = 27:1) to give **1b** (20.8 g, 60%) as a slightly yellow oil. ^{1}H NMR (CDCl$_3$, 499.1 MHz): δ 0.63 (12H, t, $J = 7$), 1.83 (8H, q, $J = 7$), 4.23 (2H, s, O*H*), 7.20 (2H, d, $J = 8$), 7.67 (1H, t, $J = 8$). ^{13}C NMR (CDCl$_3$, 125.4 MHz): δ 7.65, 34.66, 77.09, 117.72, 137.48, 161.75.

2,6-Pyridinebis(diisopropylmethanol) (1c). To a mixture of 800 mL of an ether solution of isopropylmagnesium chloride (2.0 M, 1.6 mol) and 700 mL of toluene was added 69.2 g of dimethyl 2,6-pyridinedicarboxylate (0.355 mol) in 5 portions over a period of 30 min with ice-cooling. The resulting wine red suspension was gradually heated to 110 °C (3.5 h) accompanied by the removal of ether and then kept at this temperature for 10 h. After cooling, the reaction mixture was hydrolyzed by pouring onto crushed ice. After addition of hexane (1 L), the mixture was filtered through Celite under reduced pressure. The remaining solid was washed with hexane (3 × 200 mL) and THF (5 × 200 mL). The filtrate was separated, and the organic layer was washed with water (3 × 150 mL). The aqueous layer was extracted with hexane (250 mL), and the extract was washed with water (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated in vacuo. The crude mixture was purified by chromatography on silica gel (hexane/EtOAc/^{i}PrOH = 100:4:1). The resulting product was further purified by recrystallization from heptane to give **1c** in the form of colorless prisms (20.3 g, 19%). ^{1}H NMR (CDCl$_3$, 499.1 MHz): δ 0.75 (12H, d, $J = 7$), 0.80 (12H, d, $J = 7$), 2.34 (4H, septet, $J = 7$), 7.24 (2H, d, $J = 8$), 7.66 (1H, t, $J = 8$). ^{13}C NMR (CDCl$_3$, 125.4 MHz): δ 16.72, 17.48, 34.39, 80.42, 119.07, 136.15, 159.79. IR (KBr): 3428, 3202, 2966, 2878, 1578, 1464, 1412, 1383, 1369, 1303, 1238, 1147, 1106, 1085, 1000, 917, 857, 806, 764, 669, 497. Anal. Calcd for $C_{19}H_{33}NO_2$: C, 74.22; H, 10.82; N, 4.56. Found: C, 74.42; H, 11.22; N, 4.60.

PhBi[2,6-C$_5$H$_3$N(CMe$_2$O)$_2$] (5a). To an EtOH solution (160 mL) of $PhBiBr_2$ (17.1 g, 38.4 mmol) was added an EtOH solution of NaOEt (2.0 M, 38.6 mL, 77 mmol) at −30 °C. The mixture was gradually warmed to −15 °C over a period of 1 h and then cooled again to −30 °C. An EtOH solution of **1a** (7.50 g, 38.4 mmol) was added. The mixture was gradually warmed to room temperature over a period of 5 h. EtOH was removed under reduced pressure (up to 1×10^{-3} Torr), and CH_2Cl_2 (150 mL) was added to the residue. The mixture was filtered through Celite, and the filtrate was evaporated in vacuo. To the residual solid contaminated by unreacted **1a** and a red-brown-colored material was added THF (100 mL), and the mixture was refluxed for ca. 5 min. After cooling to room temperature, the white solid was filtered and washed with THF (3 × 30 mL) and dried under reduced pressure at room temperature for 24 h. Yield: 78% (14.3 g). ^{1}H NMR (CDCl$_3$, 300.1 MHz): 1.46 (6H, s), 1.51 (6H, s), 7.20 (1H, br t, $J = 7.5$, *p*-H in Ph), 7.24 (2H, d, $J = 7.5$, 3-H in Py), 7.62 (2H, t, $J = 7.5$, *m*-H in Ph), 7.89 (1H, t, $J = 7.5$, 4-H in Py), 8.59 (2H, dd, $J = 1$, 7.5, *o*-H in Ph). ^{13}C NMR (CDCl$_3$, 75.5 MHz): 34.73, 34.84, 73.97, 120.19 (2C), 128.02, 130.72 (2C), 136.08 (2C), 139.45, 171.75, 206.97 (Bi−*C*). Anal. Calcd for $C_{17}H_{20}BiNO_2$: C, 42.60; H, 4.21; N, 2.92. Found: C, 42.13; H, 4.43; N, 2.83.

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PhBi[2,6-$C_5H_3N(CEt_2O)_2$] (5b). The compound was prepared as described for **5a** from 12.0 g (26.9 mmol) of $PhBiBr_2$ and 6.76 g (26.9 mmol) of **1a**. Recrystallization of the crude product from 1,2-dichloroethane/hexane gave colorless crystals (8.25 g, 57% yield). ^1H NMR ($CDCl_3$, 499.1 MHz): 0.55 (6H, t, *J* = 7), 0.88 (6H, t, *J* = 7), 1.73−2.01 (8H, m), 7.20 (1H, tt, *J* = 1, 7, *p*-H in Ph), 7.22 (2H, d, *J* = 7, 3-H in Py), 7.64 (2H, t, *J* = 7, *m*-H in Ph), 7.92 (1H, t, *J* = 7, 4-H in Py), 8.50 (2H, br d, *J* = 7, *o*-H in Ph). ^{13}C NMR ($CDCl_3$, 125.4 MHz): 8.04, 8.61, 36.43, 38.46, 78.98, 120.69 (2C), 128.50, 130.82 (2C), 135.05 (2C), 139.40, 169.64, 208.85 (Bi−*C*). Anal. Calcd for $C_{21}H_{28}BiNO_2$: C, 47.11; H, 5.24; N, 2.62. Found: C, 46.71; H, 5.33; N, 2.50.

PhBi[2,6-$C_5H_3N(C^iPr_2O)_2$] (5c). The compound was prepared as described for **5a** from 9.00 g (20.2 mmol) of $PhBiBr_2$ and 6.13 g (19.9 mmol) of **1c**. Recrystallization of the crude product from a 1,2-dichloroethane/heptane mixture gave colorless crystals (7.30 g, 62%). ^1H NMR ($CDCl_3$, 499.1 MHz): 0.36 (6H, d, *J* = 7), 0.64 (6H, d, *J* = 7), 0.98 (6H, d, *J* = 7), 1.07 (6H, d, *J* = 7), 2.34 (2H, sept, *J* = 7), 2.45 (2H, sept, *J* = 7), 7.21 (1H, tt, *J* = 1, 7, 4-Ph), 7.28 (2H, d, *J* = 8, 3-Py), 7.69 (2H, t, *J* = 7.5, 3-Ph), 7.88 (1H, t, *J* = 8, 4-Py), 8.56 (2H, dd, *J* = 1, 8, 2-Ph). ^{13}C NMR ($CDCl_3$, 125.4 MHz): 16.84, 18.19, 18.41, 18.59, 36.90, 37.89, 82.89, 121.51 (2C), 128.61 (1C), 130.60 (2C), 135.33 (2C), 137.48 (1C), 167.17 (2-Py), 210.43 (Bi−*C*). Anal. Calcd for $C_{25}H_{36}BiNO_2$: C, 50.76; H, 6.13; N, 2.37. Found: C, 50.55; H, 6.25; N, 2.26.

MeBi[2,6-$C_5H_3N(CMe_2O)_2$] (5d). To an EtOH solution (40 mL) of $MeBiCl_2$ (3.00 g, 10.2 mmol) was added an EtOH solution of NaOEt (2.13 M, 9.55 mL, 20.3 mmol) at 0 °C. The mixture was stirred for 40 min at 0 °C and for 80 min at room temperature. After cooling to 0 °C, an EtOH (15 mL) solution of **1a** (1.97 g, 10.1 mmol) was added to the mixture, which was stirred for 220 min at 0 °C and then at room temperature overnight. After removal of volatiles under reduced pressure, the crude product was dissolved in dichloromethane, and the solution was filtered through Celite. Removal of the solvent under reduced pressure gave **5d** as a slightly brown-colored powder (4.04 g, 96%). ^1H NMR ($CDCl_3$, 499.1 MHz): 1.21 (3H, s, Bi−Me), 1.50 (6H, s), 1.52 (6H, s), 7.27 (2H, d, *J* = 7.6, 3-Py), 7.94 (1H, t, *J* = 7.6, 4-Py). ^{13}C NMR ($CDCl_3$, 125.4 MHz): 34.04, 35.76, 63.89 (Bi−C), 73.53, 120.02, 139.44, 172.19. Anal. Calcd for $C_{12}H_{18}BiNO_2$: C, 34.54; H, 4.35; N, 3.36. Found: C, 34.65; H, 4.23; N, 3.22.

EtOBi[2,6-$C_5H_3N(CEt_2O)_2$] (5e). To an EtOH solution (80 mL) of $BiCl_3$ (3.17 g, 10.1 mmol) was added an EtOH solution of NaOEt (2.13 M, 14.1 mL, 30 mmol) at 0 °C. After stirring at 0 °C for 50 min, an EtOH (20 mL) solution of **1b** (2.54 g, 10.1 mmol) was added to the mixture, which was stirred for 20 min at 0 °C and then for 7 h at room temperature. After removal of volatiles under reduced pressure, 1,2-dichloroethane (20 mL) and heptane (10 mL) were added to the residue. The mixture was centrifuged, and the supernatant was separated. Removal of the solvent under reduced pressure and recrystallization from heptane gave **5e** as colorless crystals (3.11 g, 61%). ^1H NMR ($CDCl_3$, 499.1 MHz): δ 0.41 (6H, t, *J* = 7), 0.86 (6H, t, *J* = 7), 1.05 (3H, t, *J* = 7), 1.70−1.94 (8H, m), 4.45 (2H, q, *J* = 7), 7.29 (2H, d, *J* = 7.5), 8.00 (1H, t, *J* = 7.5). ^{13}C NMR ($CDCl_3$, 125.4 MHz): δ 7.86, 8.44, 21.73, 36.90, 38.39, 58.92, 79.52, 120.53, 139.72, 170.47. Anal. Calcd for $C_{17}H_{28}BiNO_3$: C, 40.56; H, 5.61; N, 2.78. Found: C, 40.59; H, 5.71; N, 2.95.

X-ray Crystallography. Crystal data, data collection details, and solution and refinement procedures are collected in Table 1. Data were collected on a Rigaku AFC7R diffractometer. All calculations were performed using teXsan crystallographic software package[22] unless otherwise noted. Additional comments specific to each structure follow.

5a·0.5H_2O. Small amounts of crystals were obtained from a saturated C_6D_6 solution used for NMR measurement. The crystals contained a half molecule of H_2O per **5a** molecule. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of H_2O were refined anisotropically, and the other hydrogen atoms were included in fixed positions.

5b. Crystals were obtained by recrystallization from heptane. One of the CEt_2 parts is disordered in two positions. The ratio of the population in the two positions was refined using SHELX97 crystallographic software package.[23] The final refinement was performed by using the teXsan crystallographic software package with fixed population values for the disordered atoms. Hydrogen atoms were not located on the disordered carbons. The disordered carbon atoms were refined isotropically, and the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions.

5c·CH_2Cl_2. Crystals were obtained by recrystallization from CH_2Cl_2. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions.

5e. Crystals were obtained by recrystallization from heptane. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were included in fixed positions.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **5a**, **5b**, **5c**, and **5e** and a table of hydrogen-bonding geometry for **5a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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