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Synthesis and Structure of Pentavalent Bismuth(V) Alkoxides and Ligand Redistribution Equilibria in Solution

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The six new pentavalent Bi(V) alkoxide complexes $Ph_3Bi(OR)_2$, **1**, $Ph_3BiBr(OR)$, **2**, and $Ph_4Bi(OR)$, **3** (**a**, R = C_6F_5; **b** R = C_6Cl_5) have been prepared. $Ph_4Bi(OR)$ was synthesized by alcoholysis of $BiPh_5$ with ROH. $Ph_3Bi(OR)_2$ and $Ph_3BiBr(OR)$ were products of the salt elimination reaction between Ph_3BiBr_2 and NaOR. These compounds were characterized spectroscopically and by single-crystal X-ray diffraction. In the solid state, they possess distorted trigonal bipyramidal coordination geometries. Although the mixed species $Ph_3BiBr(OR)$ may be isolated in pure form as crystalline solids, they do not exist as pure compounds in solution owing to the very rapid redistribution equilibrium $Ph_3Bi(OR)_2 + Ph_3BiBr_2 \rightleftharpoons 2Ph_3BiBr(OR)$. The equilibrium constants were measured using VT NMR spectroscopy. For comparison, the equilibrium constants for the previously unreported cross-exchange reactions between the dihalides Ph_3BiX_2 (X = F, Cl, Br) were also measured at 226 K. Trends observed in the values of K_{eq} correlate with the difference in the electronegativity of the mixed X species. The thermal stabilities of $Ph_3Bi(OR)_2$ were examined in toluene solution and in the solid state. Pyrolysis results in elimination of ROPh for both R = C_6F_5 and C_6Cl_5.

Introduction

The isolation of homoleptic Bi(V) compounds is a challenging synthetic goal. The only discrete inorganic bismuth(V) compound is BiF_5 which has been studied little, probably due to some reports that it tends to react explosively with organic compounds.[1] In contrast, the pentavalent chemistry of bismuth is well-established for organometallic compounds of the type Ar_3BiX_2 (Ar = aryl; X = F, Cl, Br, pseudohalides, Ar, etc.). The compound with X = I is notably missing from the list as addition of I_2 to Ar_3Bi results in immediate elimination of ArI to give Ar_2BiI.[2] Similar elimination reactions occur readily at ambient temperatures for BiR_5 (R = alkyl), but in remarkable work, Seppelt and coworkers have managed to synthesize, isolate, and structurally characterize the very unstable $BiMe_5$ species at low temperature.[3] Organobismuth(V) complexes have been studied as oxidants and as aryl transfer reagents.[4,5]

In approaching the challenge of creating new inorganic Bi(V) compounds, we chose to examine alkoxide ligands for two reasons: (1) the π-donation of the oxygen atoms might stabilize the high oxidation state and (2) the use of alkoxide ligands could lead to suitable sol-gel precursors for production of pentavalent bismuth oxide materials. A problematic aspect of the choice of alkoxide ligand is that alcohols are oxidized by bismuth(V).[6] Complexes have been previously synthesized which have an alkoxide ligand attached to bismuth(V), but these complexes are stabilized by chelation of the bismuth by other donor groups on the alkoxide ligand. For example, Dittes[7] et al. recently reported tris(aryl)bismuth(V) tropolonato complexes which have a seven-coordinate bismuth, and Barton, Yamamoto, and coworkers have produced hexacoordinate bismuth species.[8,9] To avoid problems with oxidation and arylation reactions, the alkoxides OR (R = C_6F_5, C_6Cl_5) were chosen for initial study. En route to producing the species $Bi(OR)_5$, we decided to establish the ability of these OR groups to support the bismuth(V) oxidation state by preparing the complexes $Ar_3Bi(OR)_2$ and $Ar_4Bi(OR)$ via salt metathesis reactions and alcoholysis, respectively. These results indeed show that bismuth(V) species with these ligands are stable. During the characterization of these compounds, the complexes gave evidence of being substitutionally labile in solution, undergoing rapid ligand redistribution reactions. While similar reactions have been reported for antimony(V) species,[10,11] this is the first such report for bismuth(V) complexes.

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Table 1. Quantities of Starting Materials, Yields, and Analytical Data

	1a	**2a**	**3a**	**1b**	**2b**	**3b**
ROH (g)	1.84	0.62	0.77	0.88	0.45	0.11
NaH (g)	0.60	0.20		0.20	0.10	
Ph_3BiBr_2 (g)	3.00	2.00		1.00	1.00	
yield (g) (%)	1.91 (47)	1.43 (59)	0.42 (72)	1.36 (88)	1.12(85)	0.18 (54)
anal. found (calcd)	C, 44.1 (44.68); H, 2.1 (1.87)[a]	C, 41.7 (40.99); H, 2.5 (2.15)[a]	C, 51.82 (51.44); H, 3.1 (2.88)	C, 37.11 (37.11); H, 1.74 (1.56); Cl, 36.43 (36.51)	C, 36.85 (36.7); H, 1.94 (1.92); Cl, 22.7 (22.57); Br, 9.9 (10.17)	C, 45.90 (46.03); H, 2.68 (2.58); Cl, 22.24 (22.65)
^{19}F NMR (ppm) in acetone-d_6	−159.2 (4), −168.3 (4), −175.7 (9)	−159.6 (4), −168.7 (4), −177.1 (9)	−166.9, −173.4, −185.35			
^1H NMR (ppm) in benzene-d_6	8.07 (2), 7.02 (m), 6.84 (m)	8.27 (2), 7.02 (m), 6.84 (m)	7.79 (d), 7.02 (m)	8.09 (2), 6.99 (3), 6.78 (3)	8.245 (2), 7.02 (m), 6.87 (m)	8.01 (d), 7.63 (m)
mp (°C)	131	124	122	155	125	145
IR (cm^{-1})	444(s), 566(w), 616(s), 644(w), 683(s), 727(s), 983(s), 1011(s), 1127(w), 1155(s), 1254(w), 1305(s), 1327(w), 1433(s), 1461(s), 1505(s), 1561(s), 1627(w), 1650(w), 3055(s)	446(s), 619(w), 644(w), 681(s), 724(s), 799(s), 984(s), 1012(s), 1043(w), 1180(w), 1160(s), 1196(w), 1261(s), 1302(m), 1325(m), 1437(s), 1465(s), 1502(s), 1560(s), 3060(m)	3051(w), 1642(w), 1161(w), 1561(s), 1489(s), 1461(w), 1433(w), 1300(w), 1239(w), 1183(w), 1161(w), 1050(w), 990(s), 844(w), 727(s), 683(w), 644(w), 611(w), 511(w), 444(s)	446.2(s), 493.7(s), 689(s), 722(s), 769(s), 982(s), 1218(w), 1353(w), 1394(s), 1437(s), 1469(s), 1528(s), 1559(s), 3057(s)	444(s), 479(s), 639(s), 679(s), 726(s), 769(s), 981(s), 1041(w), 1128(w), 1172(w), 1220(s), 1398(b), 1437(s), 1465(s), 1529(s), 1555(s), 3047(s)	3049(w), 2356(w), 1563(w), 1543(w), 1527(s), 1472(w), 1455(w), 1444(s), 1367(w), 1328(w), 1206(s), 1189(sh), 1117(w), 1050(w), 1005(w), 989(s), 844(w), 761(s), 722(s), 683(s), 644(w), 473(w), 444(s)

[a] The elemental analysis has been repeated several times giving these averaged values. The errors are due to cocrystallization of **1a** and **2a** which coexist in solution and cannot be separated completely by fractional crystallization.

Experimental Section

General Considerations. All reactions were carried out under an inert atmosphere of either argon or nitrogen using Schlenk-line, drybox, or high-vacuum techniques.[12] Solvents were freshly distilled from the appropriate drying agents prior to use: THF ($LiAlH_4$ followed by Na/Ph_2CO), toluene (Na), acetone-d_6 (molecular sieves), benzene-d_6, and toluene-d_8 (CaH_2). Ph_3BiBr_2 was synthesized according to literature procedures.[13] The phenols C_6F_5OH (PCR, Inc.) and C_6Cl_5OH were sublimed from molecular sieves under reduced pressure. Sodium hydride (Aldrich), received as a mineral suspension, was washed with hexane and dried under vacuum.[14] $BiPh_5$ was synthesized according to the literature procedure.[15] NMR spectra were recorded on a Bruker AC250 (250 MHz ^1H, 235.34 MHz ^{19}F) spectrometer; chemical shifts are reported in ppm on a scale relative to $CFCl_3$ (^{19}F NMR) as $\delta = 0$ ppm. Infrared spectra in the 400−4000 cm^{-1} region were taken on a Perkin-Elmer 1600 series spectrometer as KBr pellets. Elemental analyses (C, H) were performed on a Carlo Erba Instruments NA 1500 series 2 analyzer and by National Chemical Consulting, Tenafly, NJ (C, H, Cl, F, Br). Mass spectra were obtained on a Finnigan Mat 90.

General Synthesis of 1a,b and 2a,b. The NaOR (R = C_6F_5, C_6Cl_5) was freshly prepared for each reaction by adding a solution of the phenol in THF to NaH (excess) suspended in the same solvent. After filtration through diatomaceous earth, the solvent was removed under vacuum. The resulting NaOR was dissolved in toluene and added to a toluene solution with stoichiometric amounts of Ph_3BiBr_2. The reaction mixture was stirred at 80 °C for 12 h. After the mixture was cooled to room temperature, the solid NaBr was removed by filtration and the filtrate was concentrated. After addition of hexane to the concentrate and cooling to −10 °C, the pure product crystallized. The quantities of starting materials, yields, and analytical data for each compound can be found in Table 1.

$Ph_4BiOC_6F_5$ (3a). A solution of 0.77 g (4.1 mmol) of C_6F_5OH in toluene was added to 0.5 g (0.842 mmol) of $BiPh_5$ dissolved in toluene. The yellow reaction mixture was stirred overnight. After complete removal of the toluene, ether (15 mL) was added to the oily residue, precipitating a bright yellow solid. The product was recrystallized from toluene/ether by diffusion, forming yellow block-shaped crystals suitable for single-crystal X-ray diffraction.

$Ph_4BiOC_6Cl_5$ (3b). A solution of 0.11 g (0.42 mmol) of C_6Cl_5OH in 20 mL of toluene was added to 0.25 g (0.42 mmol) of $BiPh_5$ dissolved in 25 mL of toluene. The yellow reaction mixture was stirred overnight. After complete removal of the toluene, 40 mL of THF was added to the yellow residue and stirred for 4 h. The THF solution was filtered through diatomaceous earth. The filtrate was concentrated and placed in the freezer (−10 °C) where yellow hexagonal crystals suitable for single-crystal X-ray diffraction formed.

Thermal Decomposition. A saturated solution of each compound was refluxed in toluene for 14 h. The resulting solution was injected in a GC-MS analyzer. Under the same conditions, compound **2a** was also heated with a stoichiometric amount of tolyl bromide, followed by GC-MS.

Equilibrium Studies. Solutions of Ph_3BiBr_2, **1a**, and **1b** in benzene-d_6 were prepared in the following concentrations: For *K*(**2a**) [Ph_3BiBr_2] = 0.025 mol/L, [**1a**] = 0.025mol/L; for *K*(**2b**) [Ph_3BiBr_2] = 0.017 mol/L, [**1b**] = 0.017 mol/L. The stock solutions were then mixed in at least seven different ratios. The volumes of the mixed samples were kept constant (0.75 mL). The room-temperature ^1H NMR spectra of the equilibrium mixtures showed completely resolved peaks for the *ortho*-phenyl hydrogen atoms, which were carefully integrated to give a measurement of the concentrations of all three compounds coexisting in the equilibrium. For the determination of $\Delta H°$ and $\Delta S°$, the **1a**/Ph_3BiBr_2 and **1b**/Ph_3BiBr_2 mixtures in toluene-d_8 were measured at nine different temperatures between 178 and 312 K.

For the determination of the equilibrium constants of the triphenyl bismuth dihalide mixtures, solutions in toluene-d_8 of the following concentrations were prepared: [Ph_3BiF_2] = 0.0134 mol/L, [Ph_3BiCl_2] = 0.0143 mol/L, [Ph_3BiBr_2] = 0.0139 mol/L. Mixtures were made in NMR tubes as described above. The ^1H and ^{19}F (for fluoride-containing mixtures) spectra were recorded at 226 K.

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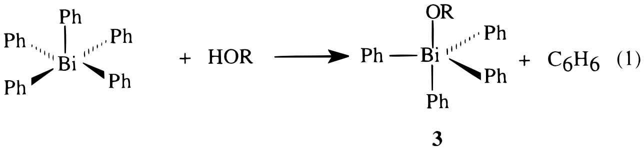
Table 2. Crystallographic Data for Compounds 1−3

	1a	**2a**	**3a**	**1b**	**2b**	**3b**
empirical formula	$C_{30}H_{15}BiF_{10}O_2$	$C_{24}H_{15}BiBrF_5O$	$C_{30}H_{20}BiF_5O$	$C_{30}H_{15}BiCl_{10}O_2$	$C_{24}H_{15}BiBrCl_5O$	$C_{30}H_{20}BiCl_5O$
fw	806.4	703.25	700.44	970.90	785.50	782.69
cryst syst	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	$P2_1/c$	$P2_1/c$	$Pna2_1$
a, Å	11.212(2)	9.313(2)	14.112(3)	16.133(3)	16.319(3)	15.918(3)
b, Å	11.705(2)	10.561(2)	17.844(4)	12.208(2)	9.901(2)	11.408(2)
c, Å	13.093(3)	13.122(3)	19.954(4)	18.416(4)	17.502(4)	15.374(3)
α, deg	102.06(3)	102.45(3)	90	90	90	90
β, deg	113.41(3)	90.56(3)	90	114.37(3)	114.64(3)	90
γ, deg	106.19(3)	115.25(3)	90	90	90	90
vol., Å^3	1411.1(5)	1132.3(4)	5024.7(19)	3303.9(11)	2570.4(9)	2791.8(10)
Z	2	2	8	4	4	4
density (calcd), Mg/m^3	1.898	2.063	1.852	1.952	2.030	1.862
abs coeff, mm^{-1}	6.340	9.605	7.077	6.174	8.949	6.817
F(000)	768	660	2688	1856	1480	1504
cryst size, mm	0.3 × 0.2 × 0.01	0.05 × 0.05 × 0.05	0.3 × 0.3 × 0.1	0.4 × 0.50 × 0.05	0.5 × 0.3 × 0.3	0.3 × 0.3 × 0.3
Θ range, deg	2.04−22.49	2.20−22.50	2.04−23.99	2.06−24.98	2.35−24.99	2.20−24.99
index ranges	$-11 \le h \le 12$ $-12 \le k \le 0$ $-13 \le l \le 14$	$-10 \le h \le 9$ $0 \le k \le 11$ $-14 \le l \le 13$	$0 \le h \le 16$ $0 \le k \le 20$ $0 \le l \le 22$	$0 \le h \le 17$ $0 \le k \le 13$ $-19 \le l \le 19$	$0 \le h \le 17$ $0 \le k \le 11$ $-20 \le l \le 18$	$-15 \le h \le 18$ $-10 \le k \le 13$ $-16 \le l \le 16$
no. of reflns colld	3902	3157	3948	4574	4001	3956
no. of ind reflns	3684 [*R*(int) = 0.0187]	2962 [*R*(int) = 0.0349]	3948	4359 [*R*(int) = 0.0402]	3833 [*R*(int) = 0.0340]	3826 [*R*(int) = 0.0303]
max, min transmission				1.0, 0.5075	1.0, 0.7086	1.0, 0.9449
data/restraints / parameters	3682/0/388	2962/0/289	3947/0/334	4359/0/388	3833/0/289	3826/1/335
goodness-of-fit on F^2	1.047	1.034	1.002	1.022	1.056	1.012
final *R* indices [$I > 2\sigma(I)$]	0.0315	0.0466	0.0454	0.0397	0.0380	0.0399
final w*R* indices [$I > 2\sigma(I)$]	0.0756	0.0819	0.0847	0.0737	0.0893	0.0729
R indices (all data)	0.0402	0.0820	0.1376	0.0945	0.0596	0.0814
w*R* indices (all data)	0.0827	0.0954	0.1092	0.0880	0.0979	0.0831
largest diff. peak and hole, e/Å^3	0.957 and −1.357	0.651 and −0.876	0.641 and −0.722	0.608 and −0.636	1.557 and −1.942	0.895 and −0.619

X-ray Crystallography. Crystals were examined under mineral oil, and the ones selected for the data collection were glued to the tip of a glass fiber and transferred to a cold nitrogen stream of a Rigaku AFC5-S four-circle diffractometer with the Texsan 5.0 software package using Mo Kα radiation ($\lambda = 0.710\,73$ Å).[16] The temperature during data collection was −50 °C. The data for **1a**, **1b**, **2b, 3a**, and **3b** were corrected empirically for absorption using ψ-scans. Structures were solved, and a full-matrix least-squares refinement on F^2 was performed using the SHELXTL-PLUS 5.0 package for PC.[17,18] Hydrogen atoms were taken into account at calculated positions. All non-hydrogen atoms were refined anisotropically. Compound **3b** was refined as a racemic twin; the absolute structure parameter is 0.522(10). Data collection parameters for all compounds are found in Table 2.

Results and Discussion

Synthesis, Structure in Solution, and Thermal Stability. There are two convenient methods synthesize pentavalent Bi(V) alkoxides, alcoholysis and salt elimination. The reaction between $BiPh_5$ and ROH (R = C_6F_5, C_6Cl_5) at ambient temperature leads to the formation of Ph_4BiOR species (see eq 1). For R = C_6F_5, a 5-fold excess of the phenol was used to achieve a high yield. The formation of **1** was not observed, even with excess phenol, showing that **3** does not undergo further alcoholysis under the given conditions. Substituted Bi(V) alkoxide complexes $Ph_3BiBr_x(OR)_{2-x}$ ($x = 0, 1$; R = C_6F_5, C_6Cl_5) can be synthesized via salt elimination reactions, if the alcohols used are stable in the presence of a bismuth(V) compound. Pentachlorophenol, pentafluorophenol, and their sodium salts are not oxidized by bismuth(V) at temperatures below 80 °C. Therefore, the reaction between Ph_3BiBr_2 and 2 equiv of NaOR in toluene according to eq 2 yields **1a** and **1b** cleanly in good yields. Using only 1 equiv of NaOR, the monosubstituted species $Ph_3BiBr(OR)$ can be synthesized as



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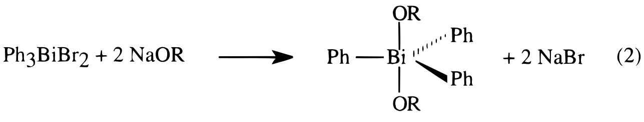

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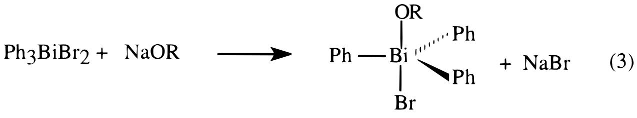

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(16) *TEXSAN 5.0, Single-Crystal Structure Analysis Software*; Molecular Structure Corp.: The Woodlands, TX, 1990.

(17) Sheldrick, G. M. *SHELXL-93*; University of Göttingen: Göttingen, Germany, 1993.

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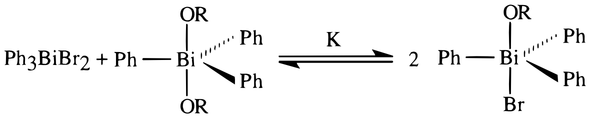
shown in eq 3, but they exist in solution in equilibrium with Ph_3BiBr_2 and $Ph_3Bi(OR)_2$ (eq 4).

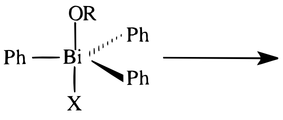


1 **2**

K(2a): R = C_6F_5
K(2b): R = C_6Cl_5 (4)

Compounds **1**−**3** represent the first examples of pentavalent Bi alkoxide complexes with a simple, nonchelating alkoxide ligand. Asthana[19] mentioned the synthesis of **1b** via reaction of Ph_3BiBr_2 with C_6Cl_5OH in the presence of triethylamine, but this synthesis could not be reproduced in our laboratory, and the characteristics described for that product do not match the results reported here.

According to Finet's suggested mechanism for arylation reactions of aromatic alcohols with bismuth(V) aryl compounds, an intermediate structure may be formed which contains a bismuth(V) center with an aryloxide ligand.[5] He suggests that these intermediates are very unstable and decompose readily to O- or C-phenylated products, depending upon the substituents on the aromatic alcohol. For electron-withdrawing groups, O-phenylation is predominant. Compounds **1a**−**2b** can be considered models of such intermediate structures in these organic reactions, because they form PhOR (R = C_6F_5, C_6Cl_5) in refluxing toluene as illustrated in eq 5. The ethers were detected with GC-MS spectrometry of the toluene solution after refluxing for 1 h.



$BiPh_2X$ + PhOR (X= Br, OR) (5)

1 or **2**

Compounds of the type $Ar_3BiX(OR')$ could eliminate biphenyl,[21] but no detectable biphenyl was observed to form from **1** and **2** in refluxing toluene after 14 h. Also, Ph_3BiBr_2 reacts to form PhBr and Ph_2BiBr in refluxing toluene.[20] A small amount of PhBr was present in the toluene solution of $Ph_3BiBr(OC_6F_5)$ after refluxing for 14 h but not in solutions of $Ph_3BiBr(OC_6Cl_5)$. This may occur because a solution of $Ph_3BiBr(OC_6F_5)$ always contains equilibrium concentrations of Ph_3BiBr_2, which would decompose to form PhBr in hot toluene. Solutions of $Ph_3BiBr(OC_6Cl_5)$ contain less Ph_3BiBr_2 since *K*(**2b**) is greater than *K*(**2a**). The formation of $PhOC_6F_5$ could also occur via reaction of PhBr with **2a**. If a such a path exists, we can expect the formation of tolylpentafluorophenyl ether ($TolOC_6F_5$) when a 1:1 solution of **2a** and tolyl bromide is heated to reflux. $TolOC_6F_5$ was not present, indicating that a bimolecular reaction between compound **2** and Ar−Br is not the source of the ether PhOR.

The thermal decomposition curves of all six crystalline compounds, **1**−**3** (TGA) were determined under Ar and Ar/O_2. The decomposition end product in Ar/O_2 after heating to 600 °C is Bi_2O_3 in all cases, suggesting that the bismuth(V) compound undergoes a reductive elimination which may be similar to the one in solution. The elimination of the ethers PhOR or bromobenzene could not be confirmed with the corresponding weight loss percentages, probably due to the extremely exothermic processes found in the DTA curves, which cause additional weight loss upon overheating of the sample.

Multinuclear NMR spectroscopy was used to probe the structures of **1**−**3** in solution. The ^1H NMR spectra show only one environment for the phenyl groups on the bismuth atom for compound **1** and two environments for **3**. A solution of compound **2** always contains equilibrium concentrations of **1**, **2**, and Ph_3BiBr_2 (see eq 4). Two of the three sets of signals in the NMR spectra correspond to **1** and Ph_3BiBr_2. The third set of peaks can be assigned to **2** and shows only one environment for the phenyl groups. The ^{19}F NMR spectra contain only peaks due to one type of pentafluorophenoxy ligand for compounds **1a** and **3a**. The ^{19}F NMR spectrum of **2a** contains signals due to **1a** and **2a** (see eq 4), each compound having one type of pentafluorophenoxy environment. The ^1H and ^{19}F NMR data combined are in agreement with the trigonal-bipyramidal coordination sphere of the bismuth atom as found in the solid state or with high fluctionality as common for five-coordinate complexes. The alkoxy and halogen ligands are situated trans to each other, and the three phenyl groups are in the equatorial plane for compounds **1** and **2**. This confirms a generally accepted rule that the most electronegative substituents always occupy the axial positions in EX_3Y_2 (E = P, As, Sb, Bi) compounds.[22] For compound **3a**, a concentration dependency of the ^{19}F shift of the *para*-flourine atom was found in toluene and acetone. The ^{19}F signals for **3a** show a higher order splitting in acetone, acetonitrile, and toluene. This complicated splitting pattern is probably due to exchange processes involving solvent molecules, since the solution color changes over time to violet in the case of acetone and to green for acetonitrile. The nature of those solution transformations will be the subject of a future publication.

Furthermore, we observed that the shift of the *ortho*-phenyl protons is temperature and concentration dependent. A similar phenomenon was observed for other R_3EX_2 (E = P, As, Sb) compounds and attributed to the changing electronegativity of E when ligand X was the same.[23] There is no obvious explanation for the change in the shift of the *ortho*-phenyl protons when E is constant and X is varied. We believe that not only the electronegativity but also possible inter- and intramolecular interactions such as H−X bonding between the substituent X and the *ortho*-hydrogen atoms could be important, because the alkoxide compounds show intermolecular interactions between the phenyl hydrogen atoms and the halogen atoms of the alkoxy group as well as the bromine in the solid state, as shown in the packing diagrams (Figures 7−9).

Solid-State Structures. Similar to many pentavalent Bi(V) compounds, the geometry about the bismuth

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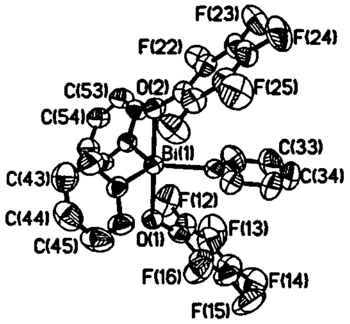

Figure 1. Structure of **1a** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

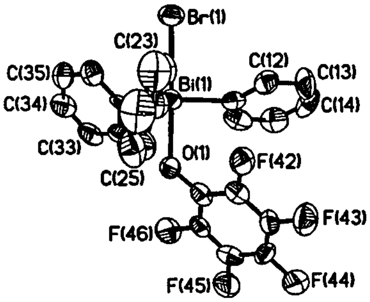

Figure 2. Structure of **2a** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

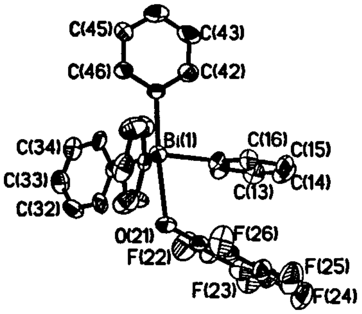

Figure 3. Structure of **3a** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

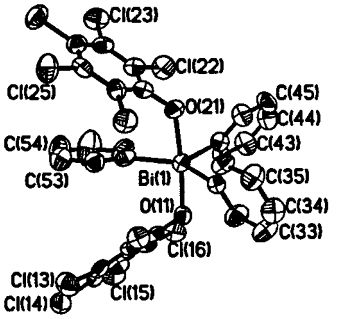

Figure 4. Structure of **1b** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

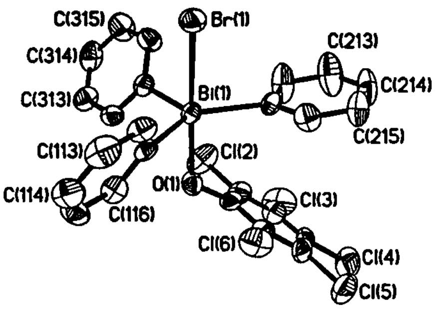

Figure 5. Structure of **2b** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

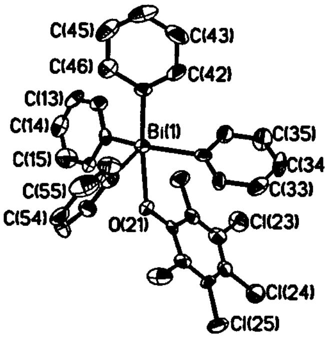

Figure 6. Structure of **3b** with thermal ellipsoid plot at 50% probability level. Hydrogen atoms have been omitted for clarity.

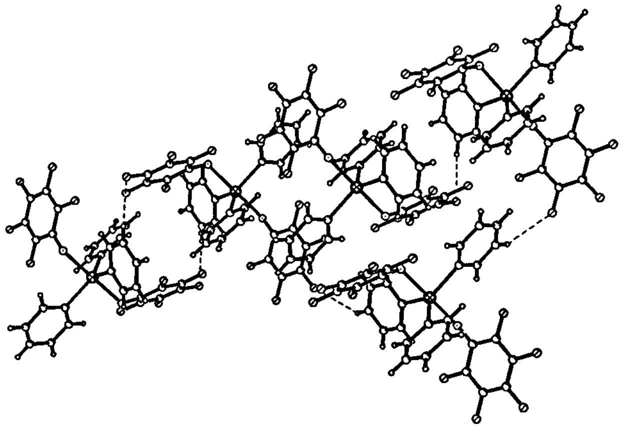

Figure 7. Packing diagram of **1a** with intermolecular interactions (H−F).

atom in the solid state is trigonal bipyramidal for all six compounds (Figures 1−6). The more electronegative substituents Br and −OR (R = C_6F_5, C_6Cl_5) occupy the axial positions and the phenyl groups are equatorial, except for the fourth phenyl group for **3a** and **3b**. The Bi−C distances are almost constant in all compounds and fall in the range of Bi−C(aryl) distances found in the literature (Table 3). The planes of two of the phenyl rings in each of the compounds **1a**, **1b**, and **2b** are rotated with respect to the equatorial plane defined by the Bi atom and the three attached phenyl carbon atoms. The phenyl ring closest to the bent alkoxy ligand(s) lies flat in the plane and has a shorter Bi−C distance.

The C−Bi−C angles deviate substantially from the ideal value of 120° (Table 3). One of the angles is always greater than 120°, which is due to the spacial requirements of the alkoxy group. The deviation is greater for the sterically more crowded C_6Cl_5. In **1b**, the two

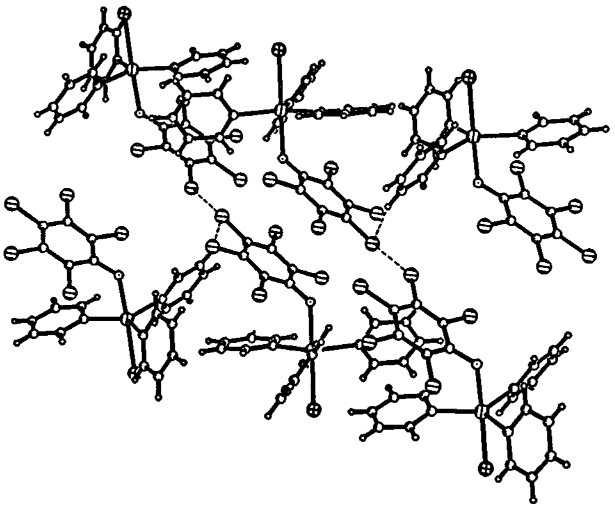

Figure 8. Packing diagram of **2b** with intermolecular interactions (Cl−H···Cl, Cl···Cl).

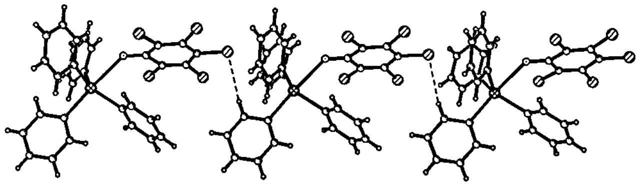

Figure 9. Packing diagram of **3b** with intermolecular interactions (C−H···Cl).

pentachlorophenoxy ligands, which are both bent toward the same equatorial phenyl group, expand the C−Bi−C angle to 142.6°. Compound **2b** has a significantly smaller C−Bi−C angle (131.7°), because there is only one C_6Cl_5 group. In all compounds, **1** and **2**, the O−Bi−O/Br angles are close to 180° (174.1(2)−179.4(2)°). The Bi−O distances are shorter than the ones found by Yamamoto for hexacoordinate Bi(V) compounds[9] and the Bi−O distance in Dittes' ditropolonato complexes.[7]

The packing in the crystal is influenced by weak halogen···hydrogen and/or chlorine···chlorine interactions. Figure 7 shows a packing diagram of compound **1a** with some of the hydrogen−fluorine contacts (F(14)···H(53a) 2.620 Å; F(24)···H(54b) 2.690 Å). Similar contacts exist in compound **2a** (F(44)−H(26b) 2.631 Å) and compound **3a** (F(24)···H(33b) 2.743 Å). For the pentachlorophenoxides, chlorine···chlorine contacts similar to those described by Desiraju for chloroaromatics can be found.[24] Desiraju interprets Cl···Cl contacts in the range from 3.27 to 4.10 Å as "short" and, therefore, structure stabilizing. He also states that in those structures where the shortest Cl···Cl contacts are at the higher end of the range, additional stabilization seems to be achieved through C−H···Cl "hydrogen bonds" in the range from 2.8 to 3.3 Å. Figure 8 illustrates both types of interactions found in compound **2b**. The shortest intermolecular chlorine−chlorine distance Cl(4)···Cl(3b) is 3.48 Å, which is stabilized by C−H···Cl "hydrogen bonds" of 2.881 Å.

In addition to those contacts, the structure is stabilized by weak π-stacking forces of the C_6Cl_5 rings, with a ring to ring distance of 3.86 Å compared to graphite sheet separation of 3.35 Å. Such π-interaction also exists in the fluorine analogue **2a**; the distance between two stacked pentafluorophenyl rings is 2.631 Å. In compound **1b**, Cl···Cl contacts and C−H···Cl hydrogen bonds were also observed (Cl(14)···Cl(24b) 3.364 Å, H(55a)···Cl(22) 2.787 Å). **3b** shows only weak intermolecular C−H···Cl hydrogen bonds (Cl(24)···H(46a) 2.895 Å).

Redistribution Reactions/Equilibrium. ^{1}H NMR spectra of a solution of single crystals of **2a** showed three sets of peaks in the *ortho*-phenyl-H region, two of which are characteristic for compounds **1a** and Ph_3BiBr_2. The third peak set was identified as that corresponding to **2a**. It was concluded that all three compounds exist in dynamic equilibrium (eq 4). This was confirmed by the presence of the signal of **2a** in the NMR spectra of various mixtures of Ph_3BiBr_2 and **1a**. The same observation was made for compound **2b**. The integrated peak intensity of the *ortho*-hydrogen atoms on the phenyl groups was used as a measurement for the equilibrium concentration of the coexisting compounds. The equilibrium occurs immediately, so that kinetic measurements were not possible. The alkoxide compounds are all similarly colored, so that no visible change results upon mixing.

Equilibrium constants for both reactions (eq 4) were calculated from NMR data according to eq 6. Constant

$$K = \frac{[\mathbf{2}]^2}{[\mathrm{Ph_3BiBr_2}]\,[\mathbf{1}]} \tag{6}$$

$K(\mathbf{2a}) = 6.5 \pm 0.3$ was calculated for reaction 4 with R = C_6F_5 in benzene at room temperature. The equilibrium constant for reaction 4 with R = C_6Cl_5 in benzene at room temperature is $K(\mathbf{2b}) = 12.8 \pm 0.5$. These values show that the equilibrium is shifted further toward the mixed-ligand product $Ph_3BiBr(OR)$ when R = C_6Cl_5. To understand this tendency, variable-temperature NMR spectroscopy was used to determine $\Delta H°$ and $\Delta S°$ for the equilibria. The variable-temperature measurements were carried out in deuterated toluene, which has a lower freezing point than benzene. The room-temperature equilibrium constants for toluene solutions are on the same order of magnitude as, but not identical to, the ones in benzene ($K(\mathbf{2a}) = 7.4$ and $K(\mathbf{2b}) = 16.9$).

Figure 10 shows the logarithmic dependence of K on $1/T$ for the formation of **2a** and **2b** in toluene. A simple curve fit was applied for the calculation of $\Delta H°$ and $\Delta S°$.

$$\ln K(\mathbf{2a}) = (87.8\ \mathrm{J\ mol^{-1}})/T + 1.71\ \mathrm{J\ mol^{-1}}$$

$$\ln K(\mathbf{2b}) = (536\ \mathrm{J\ mol^{-1}})/T + 0.993\ \mathrm{J\ mol^{-1}}$$

$$(R^2 = 0.998) \quad (R^2 = 0.991)$$

$$\Delta H°(\mathbf{2a}) = -730\ \mathrm{J\ mol^{-1}} \quad \Delta H°(\mathbf{2b}) = -4457\ \mathrm{J\ mol^{-1}}$$

$$\Delta S°(\mathbf{2a}) = 14\ \mathrm{J\ mol^{-1}\ K^{-1}} \quad \Delta S°(\mathbf{2b}) = 8\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

In both reactions, the entropy change is essentially zero, as expected. The enthalpy changes are also small,

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[24] (a) Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222. (b) Desiraju, G. R.; Parthasarathy, R. *J. Am. Chem. Soc.* **1989**, *111*, 8725.

Table 3. Selected Bond Distances (Å) and Angles (deg)

	1a	2a	3a	1b	2b	3b
Bi–C	2.193(7)	2.195(14)	2.200(11)	2.188(10)	2.189(9)	2.181(14)
	2.203(8)	2.220(13)	2.233(12)	2.188(10)	2.214(9)	2.209(12)
	2.196(7)	2.212(14)	2.222(13)	2.209(11)	2.215(9)	2.21(2)
Bi–O	2.228(5)	2.235(9)	2.544(7)	2.250(7)	2.230(6)	2.543(9)
	2.212(5)			2.244(7)		
Bi–Br/C		2.726(2)	2.257(11)		2.7417(14)	2.22(2)
C–Bi–C	121.8(3)	123.0(5)	115.9(4)	142.6(4)	131.7(3)	114.8(5)
	119.3(3)	119.5(5)	120.1(4)	113.4(4)	116.1(3)	107.8(6)
	119.0(3)	116.9(5)	116.7(4)	103.9(4)	112.2(3)	128.5(5)
C–Bi–O	87.4(2)	88.5(4)	78.3(4)	90.4(3)	91.4(3)	78.1(4)
	91.1(2)	88.7(5)	81.7(4)	91.3(3)	88.2(3)	80.1(4)
	92.7(2)	84.5(4)	83.0(4)	88.1(3)	89.3(3)	82.4(5)
C–Bi–O/Br/C	87.6(2)	91.3(3)	100.5(4)	89.5(3)	87.5(2)	100.7(5)
	89.2(2)	94.2(4)	100.1(4)	94.4(3)	91.2(2)	101.5(5)
	91.9(2)	92.5(3)	96.5(4)	88.5(3)	92.9(2)	97.6(5)
O–Bi–O or Br	179.4(2)	176.6(3)	174.9(4)	174.1(2)	177.8(2)	175.4(4)

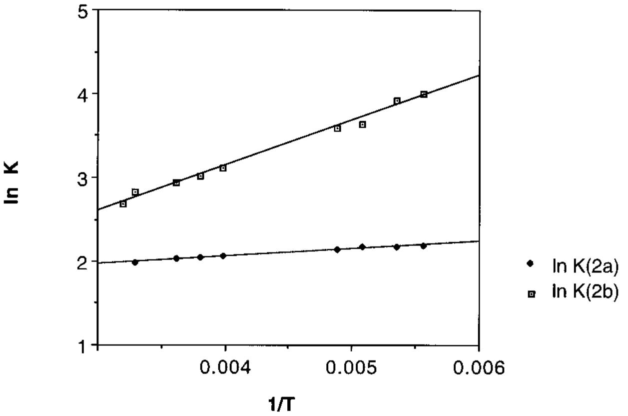


Figure 10. ln K as a function of $1/T$ for equilibrium 4 in toluene.

as anticipated from a simple bond breakage and formation analysis, with $\Delta H°$ for the formation of **2b** being about 6 times greater than the one for **2a** formation. Moreland et al. observed similar redistribution reactions for pentavalent organoantimony dihalides. They concluded that the equilibrium constants are influenced by the R group and by the electronegativity difference of the two halides.[10] Keeping the R group constant (R = Ph), we investigated the influence of the ligand electronegativity on the redistribution equilibria. Since pentavalent organobismuth dihalides also undergo redistribution reactions (see eq 7) with each other, mixed toluene solutions of triphenyl bismuth dihalides Ph_3BiX_2 (X = F, Cl, Br) were analyzed by NMR spectroscopy. At room temperature, broad and unresolved

$$Ph_3BiX_2 + Ph_3BiY_2 \xrightleftharpoons{K_{eq}} 2Ph_3BiXY \qquad (7)$$

peaks were observed in the *ortho*-phenyl-hydrogen region. At 226 K, the three signals are separated for all three mixtures. Two signals correspond to the parent dihalides, and the third one was attributed to the mixed-halide species. In Table 4, the equilibrium constants for the dihalides corresponding to eq 7 are listed at 226 K as well as the values for the equilibrium constants $K(\mathbf{2a})$ and $K(\mathbf{2b})$ at 226 K.

It was found that the change in the free energies of the equilibria show a linear dependence on the difference of the Pauling-electronegativity (EN) between the ligands X and Y, which is illustrated in Figure 11 as a function of [EN(X) − EN(Y)] vs $\Delta G°$. Making the very simplified assumption that this relationship still holds for the complex OR ligands, this graph and the values for $K(\mathbf{2a})$ and $K(\mathbf{2b})$ at 226 K can be used to estimate the effective group electronegativity of OC_6F_5 and OC_6Cl_5. By interpolation, EN(OC_6F_5) equals 3.32 and EN(OC_6Cl_5) is 3.75. To our knowledge, the group electronegativities for those two −OR groups (OC_6F_5 and OC_6Cl_5) have not been measured. The tabulated group electronegativity for OC_6H_5 is 3.5, about midway between OC_6F_5 and OC_6Cl_5. Since OC_6H_5 is oxidized by Bi(V) compounds, it is not possible to obtain an experimental value for that group for comparison. We would have expected OC_6F_5 to be more electronegative as a group than OC_6Cl_5; but since OC_6Cl_5 is very bulky compared to OC_6F_5, as shown by the Bi–O distances for **1a** and **1b** (Table 3), steric factors may also strongly influence the redistribution equilibrium constant.

Table 4. Electronegativity Differences and K_{eq} at 226 K for Possible X/Y Combinations

X	Y	EN(X) − EN(Y)	K_{eq} (226 K)
Cl	F	1.0	38.04 (±1.2)
Br	F	1.2	59.75 (±4)
Br	Cl	0.2	2.92 (±0.18)
Br	OC_6F_5	0.52[a]	8.14
Br	OC_6Cl_5	0.95[a]	28.94

[a] Extrapolated from the curve in Figure 11.

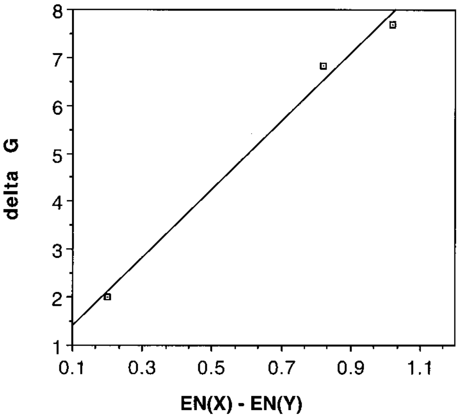
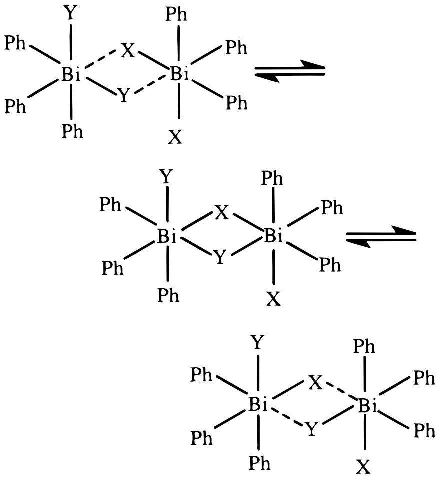


Figure 11. $\Delta G°$ vs the electronegativity difference of X and Y.

Studies on $R_3E(X)(Y)$ (E = As, Sb) compounds allowed the determination of equilibrium constants for different

R groups (R = Me, Ph, Bz) and a number of halogen combinations (X/Y = F, Cl, Br, I) in chloroform.[10] For $Me_3Sb(X)(Y)$ equilibria, a temperature dependence of K was reported. The general tendencies in these systems vary from the data reported here, which may be due to the different solvent and different R groups. A direct comparison to the Sb system is not possible since Me_3BiX_2 compounds are not stable. The formation of a bridged dimer structure, as shown in eq 8, is a reasonable explanation for these redistribution reactions since they occur in benzene and toluene, which do not support ionic structures, and no free fluoride or $-OR_f$ groups were observed in the ^{19}F NMR spectra. The formation and dissociation of the dimer must be fast on the NMR time scale.



(8)

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Supporting Information Available: Tables of thermodynamic data for Figure 10 and atomic coordinates, bond lengths and angles, and anisotropic displacement parameters and ORTEP diagrams for compounds **1**, **2**, and **3** (34 pages). Ordering information is given on any current masthead page.

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