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Bismuth Aryloxides

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The synthesis and full characterization (mp, NMR, UV/vis, FTIR, and elemental analysis) of 13 bismuth aryloxides are reported. We have prepared bismuth aryloxides with alkyl, aryl, and allylic substituents on the aryl rings. Eleven of these bismuth aryloxides have been characterized with single crystal X-ray diffraction methods. Bismuth−donor interactions (donor = aryl, methoxy) are observed in several cases. Three unexpected bismuth oxo aryloxides (**6c**, **9c**, **11c**) were also isolated. Complex $C_{77}H_{102}Bi_4Br_6O_8$ (**6c**) results from apparent C−H activation and Bi−C bond formation as a sideproduct in the synthesis of $Bi(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}BrC_6H_2)_3$ (**6**). Cluster **9c** has a $Bi_{32}O_{56}$ core, and cluster $C_{90}H_{90}Bi_4Li_2O_{12}$ (**11c**) is the second lithium bismuth oxo cluster reported to date.

I. Introduction

There has been a recent surge of interest in the chemistry of bismuth, especially the chemistry of bismuth alkoxides. Bismuth is an important component of oxide ion conductors,[1] ferroelectric materials,[2,3] catalysts,[4−6] superconductors,[7,8] and other advanced materials,[9,10] and bismuth alkoxides have been extolled as promising precursors for such bismuth oxide-containing materials.[10−12] Bismuth compounds are used for treatment of gastrointestinal disorders,[13] radioisotope therapy,[14] and many other pharmaceutical applications.[13] The low toxicity of bismuth has led to its use as a lead replacement in many materials.[15] There is also interest in the fundamental chemistry of this heavy main group element, which frequently differs from the chemistry of its lighter congeners.[16−18]

Our group has been interested for some time in the chemistry of bismuth alkoxides,[4,19−26] especially as models for the Bi/Mo oxide SOHIO catalysts that are used for propene/propane oxidation and ammoxidation.[22] We reviewed current knowledge pertaining to the role of bismuth in the SOHIO process and concluded that both its exact role

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and the mechanistic details remain controversial.[4] It is certainly involved in the initial activation of propene; however, its oxidation state over the course of this activation remains a subject of discussion. We communicated our observations of bismuth−oxygen bond homolysis in homogeneous bismuth aryloxide complexes, which supports the intervention of the Bi(II) radical in the SOHIO system.[22]

The role of bismuth in later oxidation/ammoxidation steps such as hydrogen abstraction is unclear,[4] but there have now been multiple reports of homogeneous complexes in which bismuth appears to intramolecularly abstract hydrogens to form new bismuth−carbon bonds.[27,28] We noted a similar reaction in our laboratories[4] and herein will provide more detailed information concerning the crystal structure of the resulting ladder complex.

Though bismuth aryloxides appear to mimic both structural and functional aspects of the bismuth active site in the SOHIO system, very few bismuth aryloxides have been reported.[29−33] Indeed, the entire field of bismuth alkoxide chemistry is rather small, as was brought out in a recent review.[10]

Herein, we will describe the synthesis and characterization of a series of bismuth aryloxides, as well as some unexpected side products that were found along the way. These complexes can be used as straightforward homogeneous model systems for the bismuth site, with substituents on the aryl ring that are easily adjusted to control their stability. Many of these complexes will be used in future studies of Bi(II) radical formation by Bi−O bond homolysis and hydrogen abstraction from propene-like substrates. These complexes may also have utility as precursors for bismuth oxide materials.

II. Background of Bismuth Aryloxides

The first crystallographically characterized bismuth aryloxide, $\mathrm{Bi(O\text{-}2,6\text{-}Me_2C_6H_3)_3}$ **1**, was structurally characterized by Evans and co-workers in 1989.[31] It was synthesized by salt metathesis, according to eq 1.

$$\mathrm{BiCl_3 + 3MOAr \xrightarrow[M = Li,\ Na;\ Ar = aryl]{} Bi(OAr)_3 + 3MCl} \qquad (1)$$

An analogue, $\mathrm{Bi(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_3}$ **2**, was mentioned in an article by Sauer et al. in 1990, but no characterization data were supplied.[34] Sauer et al. used the bismuth amide $\mathrm{Bi[N(SiMe_3)_2]_3}$[35] as a precursor, to which they added the appropriate phenol (eq 2). We have primarily used these same two methods in order to synthesize our bismuth aryloxides.

$$\mathrm{Bi(NR_2)_3 + 3HOAr \xrightarrow[R = Me\ or\ SiMe_3;\ Ar = aryl]{} Bi(OAr)_3 + 3HNR_2} \qquad (2)$$

Bismuth catecholates have been reported, but with limited characterization.[29,36] Whitmire et al. prepared the halide-substituted $\mathrm{Bi(OC_6F_5)_3}$.[30] More exotic bismuth aryloxides include bismuth calixarenes[20,21,23−26] and a tripodal bismuth aryloxide that forms an inverted sandwich structure with toluene as the π-donating ligand.[32] Several bismuth oxo aryloxide clusters have been reported along with the corresponding bismuth aryloxides.[10,37,38]

III. Results and Discussion

We have synthesized and fully characterized 13 bismuth aryloxides. They will be discussed in three sections. Bismuth aryloxides with alkyl substituents include the following: $\mathrm{Bi(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_3}$ **2**, $\mathrm{Bi(O\text{-}2\text{-}{}^{t}BuC_6H_4)_3}$ **3**, $\mathrm{Bi(O\text{-}2,4,6\text{-}{}^{t}Bu_3C_6H_2)_3}$ **4**, $\mathrm{ClBi(O\text{-}2,4,6\text{-}{}^{t}Bu_3C_6H_2)_2}$ **5**, $\mathrm{Bi(O\text{-}2,6\text{-}{}^{i}Pr_2\text{-}4\text{-}BrC_6H_2)_3}$ **6**, $\mathrm{Bi(O\text{-}2,6\text{-}{}^{i}Pr_2\text{-}4\text{-}ClC_6H_2)_3}$ **7**, and $\mathrm{Bi[O\text{-}2,6\text{-}{}^{i}Pr_2\text{-}4\text{-}(OCH_3)\text{-}C_6H_2]_3}$ **8**. Bismuth aryloxides with aromatic substituents include the following: $\mathrm{Bi[O\text{-}2,6\text{-}(C_6H_5)_2C_6H_3]_3}$ **9** and $\mathrm{Bi[O\text{-}2,6\text{-}(CH_2C_6H_5)_2C_6H_3]_3}$ **10**. Bismuth aryloxides with allyl substituents include the following: $\mathrm{Bi[O\text{-}2\text{-}(CH_2CH{=}CH_2)\text{-}C_6H_4]_3}$ **11**, $\mathrm{Bi[O\text{-}2\text{-}(CH{=}CHCH_3)C_6H_4]_3}$ **12**, $\mathrm{[Bi[O\text{-}2\text{-}OCH_3\text{-}6\text{-}(CH_2CH{=}CH_2)C_6H_3]_3]_2}$ **13**, and $\mathrm{[Bi[O\text{-}2\text{-}OCH_3\text{-}4\text{-}(CH_2\text{-}CH{=}CH_2)C_6H_3]_3]_2}$ **14**. We have also isolated three bismuth oxo aryloxide clusters as side products from the reactions to make the corresponding bismuth aryloxides. They are $\mathrm{\{(ArO)_2Bi(\mu_3\text{-}O)Bi(\mu_2\text{-}O\text{-}4\text{-}Br\text{-}2\text{-}{}^{i}Pr\text{-}6\text{-}[(C{=}CH_2)CH_2]\ C_6H_2\text{-}1{:}2\kappa^2O,\ 2\kappa C\}_2}$ (Ar = $\mathrm{4\text{-}Br\text{-}2,6\text{-}{}^{i}Pr_2C_6H_2}$) ($\mathrm{C_{77}H_{102}Bi_4Br_6O_8}$, **6c**), $\mathrm{Bi_{32}O_4(OH)_4(O\text{-}2,6\text{-}Ph_2C_6H_3)_{12}}$ ($\mathrm{C_{216}H_{160}Bi_{32}O_{56}}$, **9c**), and $\mathrm{Li_2Bi_4(\mu^3\text{-}O)_2[O\text{-}2\text{-}(CH_2CH{=}CH_2)C_6H_4]_{10}}$ ($\mathrm{C_{90}H_{90}\text{-}Bi_4Li_2O_{12}}$, **11c**).

All bismuth tris-aryloxides in this paper were synthesized by the exchange reaction between bismuth amide and the appropriate phenol (eq 2). Some were also synthesized by salt metathesis (eq 1), to obtain the identical products. The exchange reaction method was preferred because the products often precipitate out from the reaction mixture, facilitating isolation. The reaction time varies from 4 to 12 h. The workup is simple filtration and washing, and yields ranged from 40 to 88%.

The key factor of these reactions is how to favor product formation. The selection of suitable solvents can help to precipitate out the products and drive the reaction to completion. For example, the reaction of 2,6-diisopropyl-4-methoxyphenol and bismuth amide $\mathrm{Bi[N(SiMe_3)_2]_3}$ in pentane led to a mixture of product and starting materials. In hexanes, this reaction went smoothly with the precipitation of the product after 1 day.

Both the electronic and steric properties of the phenols can affect the reaction. An advantage of choosing bismuth aryloxides as the model complexes is that it is easy to change the properties of the phenols by changing the substituents on the phenyl ring.

The formation of the trisubstituted bismuth compounds was confirmed spectroscopically. In the ^{1}H NMR spectra of the products, there is no OH peak and the remaining resonances are shifted from those of the starting phenols. We did not observe exchange of free phenol into bismuth

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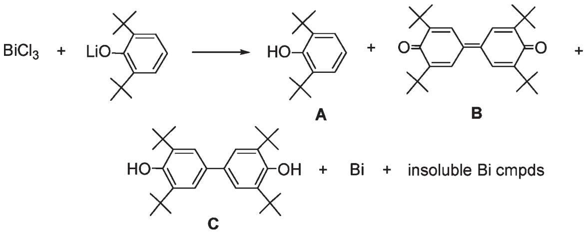
aryloxides. The IR spectra of the bismuth compounds display essentially the absorption bands of the ligands except for the OH stretch (at ~3500 cm^{-1}). The UV/vis spectra show peaks for the absorption from the phenyl rings of the phenoxy ligands. When the ligands have substituents that can form a conjugated system with the phenyl ring, the wavelengths of the peaks become longer, as expected. Eight of the bismuth aryloxides (**2**, **5**, **6**, **7**, **9**, **10**, **13**, **14**) have also been characterized by single crystal X-ray diffractometry (vide infra).

A. Ligands with Alkyl Substituents. After repeating the synthesis of $Bi(OAr)_3$ **1** (literature yield 80%),[31] we synthesized bismuth aryloxide **2** using either salt metathesis or alcohol exchange. Both methods were successful, with alcohol exchange providing the higher yield of 69%. We obtained X-ray quality crystals by crystallization in THF at −35 °C, and the crystal structure is shown in Figure 1. The structure is very similar to that of **1**,[31] with a monomeric trigonal pyramidal geometry, Bi−O bond lengths of 2.119(3), 2.092(3), and 2.082(3) Å, and O−Bi−O bond angles of 94.06(7), 95.74(6), and 96.35(7)° (see Table 1 for comparisons). The small O−Bi−O bond angles are typical of Bi(III) complexes and have been discussed previously.[19,31]

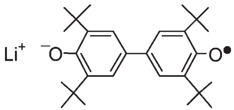
We have found that the steric bulk of the ligand is a primary determinant of its ability to form isolable $Bi(OAr)_3$ complexes. The asymmetric ligand 2-*tert*-butylphenol, for example, had similar size and similar reactivity to the diisopropylphenol. $Bi(O^tBuC_6H_4)_3$ was obtained in 88% yield. Attempts to make the unsubstituted analogue $Bi(OPh)_3$ led to white insoluble material.

When we increased the bulkiness of the ligand, by putting ^{t}Bu groups in both *ortho* positions, the reaction was very different. As described in our previous communication,[22] we observed multiple color changes of the reaction mixture (yellow, red, deep green with black precipitate) and identified di-*tert*-butylphenol **A**, diphenoquinone **B**, and diol **C** as the organic products (eq 3).



(3)

All diamagnetic products were observed by NMR, and the radical anion **D** was observed by electron paramagnetic resonance (EPR). Mass balance showed that 30% of the ligands were converted to oxidation products. The remainder was observed either as an insoluble black precipitate, or else as a combination of black precipitate and a mirror around the inside of the reaction vessel.



D

Analogous decomposition products (identified by comparison with authentic samples) were observed when $Bi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_3$ **2** was heated, but only in trace quantities. After heating for one week at 135 °C, only 20% decomposition of $Bi(OAr)_3$ was observed. In the decomposition products, we observed trace diphenoquinone, 10% of the corresponding diol, and 90% phenol.

A1. *Para*-Substituted 2,6-di^{t}Bu Ligands. In order to determine the effect of changing electronics on the bismuth−oxygen bond homolysis reaction, we attempted to synthesize the $Bi(OAr)_3$ complexes with ^{t}Bu groups in the *ortho* positions and various *para* substituents. In the cases of $HO\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}RC_6H_2$ where R = H, Br, Cl, OMe, or NMe_2 the $Bi(OAr)_3$ complexes were neither isolated nor observed at room temperature due to fast decomposition. When the reactions of bismuth amide with corresponding phenol were tried, there was no reaction at room temperature. If heated to 45 °C, decomposition of bismuth amide was observed. In all cases, free phenol and uncharacterized black solid were decomposition products, while for R = Br, diphenoquinone was also observed by ^{1}H NMR and X-ray.

In the case of the *para*-^{t}Bu group, salt metathesis of $BiCl_3$ with $LiO\text{-}2,4,6\text{-}^tBu_3C_6H_2$ yielded both $Bi(O\text{-}2,4,6\text{-}^tBu_3C_6H_2)_3$ **4** (the composition of **4** was inferred by analogy to the other bismuth aryloxides; the compound was not sufficiently stable for either X-ray or elemental analysis) and $Bi(O\text{-}2,4,6\text{-}^tBu_3C_6H_2)_2Cl$ **5**. To isolate **4**, a 2:1 mixture of phenolate and $BiCl_3$ was stirred at room temperature for 1 h and, then, filtered and recrystallized at −35 °C. When a 1:1 mixture of phenolate and $BiCl_3$ was stirred for 12 h at room temperature, only **5** was isolated. Variation of either the stoichiometry or the reaction time led to unsatisfactory results (either black solid or intractable mixtures). With the bismuth amide exchange method (eq 2), there was no reaction at room temperature. Apparently the trisubstituted complex **4** is less stable than the disubstituted complex **5**, but both are unstable in solution. The decomposition of **5** again proceeds through Bi−O bond homolysis to form the phenoxy radical, which was directly observed by UV/vis and EPR spectroscopies.[39] The $\bullet O\text{-}2,4,6\text{-}^tBu_3C_6H_2$ radical is quite stable, and an independent sample was also synthesized by literature procedures[39,40] to confirm its spectroscopic identification.

Recrystallization in pentane at −35 °C led to the isolation of X-ray quality crystals of complex **5** (see Figure 1). Again, the Bi−O bond distances and angles are in the normal range. Table 1 summarizes the Bi−O bond distances and angles. The Bi−Cl bond length in **5** is 2.492(1) Å and likely covalent in nature. In Limberg et al.'s bimetallic compound $[Cp_2Mo(\mu\text{-}OEt)_2Bi(OEt)_2Cl]$, the terminal Bi−Cl bond is 2.918(4) Å.[41] Unlike the bismuth aryloxy halides of Norman and co-workers,[42] $Bi(OAr)_2Cl$ **5** is neutral, monomeric, and tricoordinated. This is due to steric bulk of the ligand; $Sb(O\text{-}2,4,6\text{-}^tBu_3C_6H_2)Cl_2$ was also reported to be monomeric.[42]

A2. Para-Substituted 2,6-di-^{i}Pr Ligands. Since the di-*tert*-butylphenols led to unstable bismuth aryloxides, we

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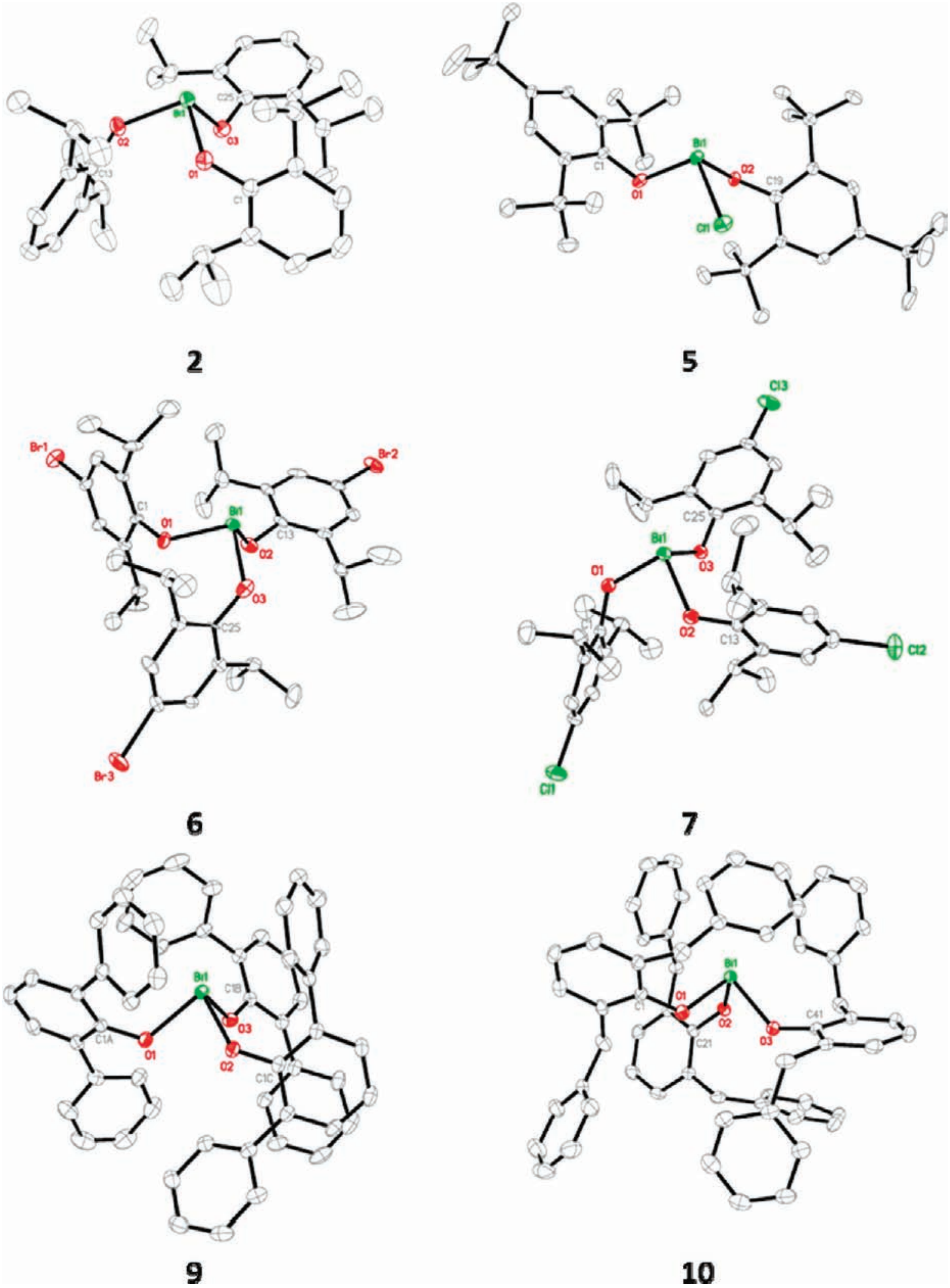

Figure 1. Diagram of the molecular structures of **2**, **5**, **6**, **7**, **9**, and **10**, all monomeric bismuth aryloxides. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms have been omitted for clarity.

next prepared bismuth complexes with 2,6-diisopropyl-4-bromophenol, 2,6-diisopropyl-4-chlorophenol, 2,6-diisopropylphenol, and 2,6-diisopropyl-4-methoxyphenol. The phenols HO-2,6-^{i}Pr$_2$-4-RC$_6$H$_2$ for R = H, Br,[43] Cl,[44] and OMe[45,46] were either obtained commercially

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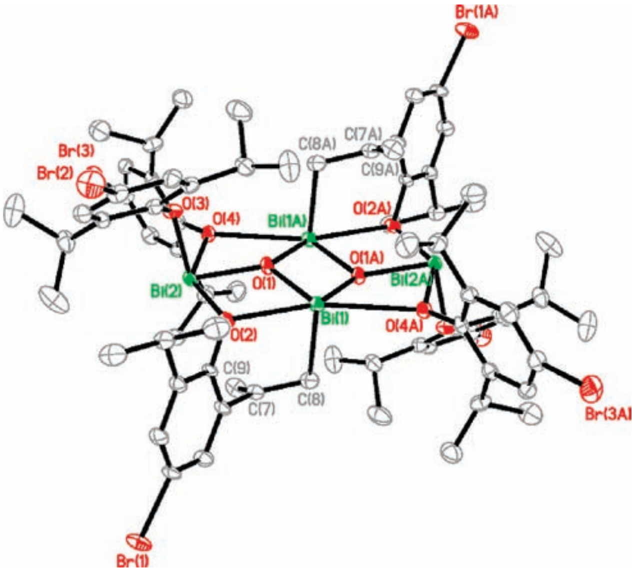


Figure 2. Diagram of the molecular structure of **6c** (30% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

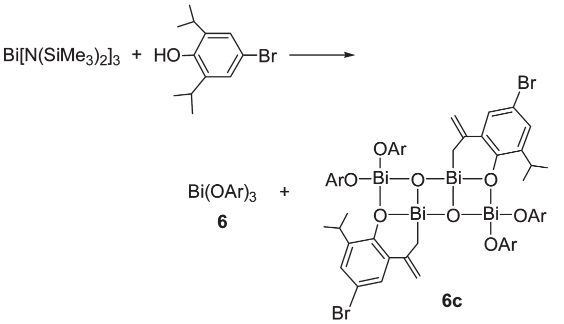
Table 1. Comparison of Important Bond Lengths (Å) and Bond Angles (deg)

compound	average Bi−O (aryloxy)/Å	average O−Bi−O/(deg)
1[31]	2.091(5)	92(2)
2	2.09(2)	95(2)
5	2.093(3)	96(8)
6	2.065(9)	94(3)
7	2.065(9)	94(3)
9	2.11(1)	86(2)
10	2.10(2)	91(8)
13	2.140(4)	85.1(3)
14	2.177(9)	88.55(78)

(R = H) or synthesized by literature procedures. All bismuth aryloxides Bi(O-2,6-^{i}Pr-4-RC$_6$H$_2$)$_3$ (R = H **2**, Br **6**, Cl **7**, OMe **8**) were stable at room temperature and characterized by mp, elemental analysis, ^{1}H and ^{13}C NMR, UV/vis, and IR spectroscopies. The complexes were made by alcohol exchange for the amido group of Bi[N(SiMe$_3$)$_2$]$_3$ with isolated yields of 45−78%. The crystal structures of **6** and **7** were determined (Figure 1) and found to be analogous to the structures of **2** and Bi(O-2,6-Me$_2$C$_6$H$_3$)$_3$.[31] Selected bond angles and distances are summarized in Table 1.

As the *para* substituent was changed from bromo to H, Cl, and then methoxy, the precipitation of product (eq 2) appeared to slow. Whereas the product precipitated from solution after only 1 h in the *para*-bromo case, it took 24 h to appear for R = OMe. This trend is probably due to a combination of electronic and solubility effects.

A3. Isolation of C$_{77}$H$_{102}$Bi$_4$Br$_6$O$_8$ 6c—A Cluster with New Bi−C Bonds. During the isolation of Bi(O-2,6-^{i}Pr$_2$-4-BrC$_6$H$_3$)$_3$ **6**, an unexpected side product was obtained (eq 4). Treatment of Bi[N(SiMe$_3$)$_2$]$_3$ with 3 equiv of 2,6-diisopropyl-4-bromophenol (HOAr) in pentane at room temperature gave a yellow cloudy solution after 12 h. Bi(OAr)$_3$ **6** was isolated from this reaction mixture as an air sensitive yellow powder. Upon filtering and concentration of the reaction mixture, crystals of an unexpected byproduct were also obtained from the mother liquor. Figure 2 shows the crystal structure of {(ArO)$_2$Bi(μ_3-O)Bi(μ_2-O-4-Br-2-^{i}Pr-6-[(C=CH$_2$)CH$_2$]C$_6$H$_2$-1:2κ^2O, 2κC}$_2$ (Ar = 4-Br-2,6-^{i}Pr$_2$C$_6$H$_2$) **6c** with new Bi−C bonds formed by activation of isopropyl substituents of the aryl ligands. Single crystals of compound **6c** were obtained twice and checked by independent crystallographers. However, only a few crystals were obtained each time, and we have not yet succeeded in optimizing conditions to increase the yield. Allylic contaminants were not detected in the starting phenol, and attempts to produce analogues of **6c** using phenols with *ortho*-allylic substituents were unsuccessful.



(4)

The structure of **6c** may be compared to that of the ladder complex reported by Uchiyama and co-workers,[47] in which Martin's ligand (−C$_6$H$_4$C(CF$_3$)$_2$O−)[48] provides Bi−C and Bi−O bonds. Most bond lengths and angles fall within normal parameters.

The most notable structural aspect of compound **6c** is the Bi$_4$O$_6$ central core, which exemplifies a structural motif found in many bismuth oxo alkoxide clusters.[20,21,24,25,37,49,50] The central centrosymmetrical four membered ring is not planar; the dihedral angle between the Bi(1)O(1)Bi(2) and Bi(1)O(2)Bi(2) planes is 11.9°. However, the central Bi$_4$O$_6$ core is planar within 0.053 Å. Therefore, although O(1) and O(1A) are slightly above and below (0.204(3) Å) the average Bi$_4$O$_6$ plane, the central Bi$_4$O$_6$ core can be considered to be coplanar, rather than forming the more common twisted framework. The terminal aryloxy bonds are perpendicular to the Bi$_4$O$_6$ plane, with the rings on O(3) and O(4) being mutually perpendicular. A similar planar structure was observed in a set of Andrews Bi(OCH(CF$_3$)$_2$)$_3$L$_3$ (L = thf, Et$_2$O, or tmeda) complexes,[50] as well as in the Bi$_2$Mo$_2$O$_6$ core of our mixed-metal bismuth molybdenum calixarene cluster.[26]

There are two types of bismuth atoms, Bi(1) and Bi(2). The Bi(1) atom is five coordinate, and its coordination can be described as a pentagonal pyramid with one empty equatorial coordination site. Four oxygen atoms and a vacant coordination site are at equatorial positions, with one carbon in the apical position. The angles of C(8)−Bi(1)−O(1), C(8)−Bi(1)−O(1A), C(8)−Bi(1)−O(2), and C(8)−Bi(1)−O(4A) are 88.91(16), 93.99(16), 83.14(15), and 91.90(15)°, respectively.

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Table 2. Examples of Bismuth−Centroid and Bi−C Distances in Bi−Arene Interactions

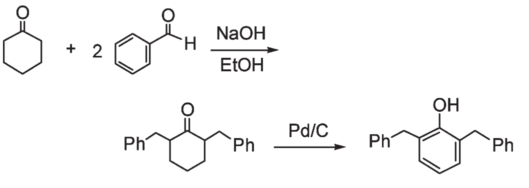
compound	shortest Bi−C distances (Å)	bismuth−centroid distances (Å)	ref
$Bi(O\text{-}2,6\text{-}Ph_2C_6H_3)_3$, **9**	3.115, 3.096, 3.083	3.479, 3.466, 3.341	
$Bi(O\text{-}2,6\text{-}Bz_2C_6H_3)_3$, **10**	3.376, 3.373, 3.155	3.900, 3.146, 3.830	
$Bi(OCPh_3)_3$	3.179, 3.157, 3.052	3.93, 3.84, 3.71	19
$\{N(OAr)_3Bi\}_2$(toluene)	3.524	3.07	32
$[Bi(OC_6F_5)_2(\mu\text{-}OC_6F_5)(C_7H_8)]_2$	3.162	2.958	30

The Bi(2) atom is coordinated only to four oxygens. Three Bi−O bonds are in the plane of the Bi_4O_6 core with angles of 68.12(12)−73.45(10)° between the bonds, and the fourth Bi−O bond is almost perpendicular to this plane (O(3)−Bi(2)−O(2), O(3)−Bi(2)−O(1), and O(3)−Bi(2)−O(4) are 91.23(11), 93.50(12), and 90.16(11)°, respectively).

The chelate six-membered ring Bi(1)O(2)C(1)C(2)C(7)C(8) is in an approximate boat conformation. The C(7)−C(9) double bond distance is 1.339(7) Å, and the ^1H NMR spectrum shows methylene peaks at 4.76 and 4.36 ppm. This double bond activates the hydrogen atoms on the neighbor carbon C(8); therefore, the group of C(8), C(7), and C(9) is similar to an allyl. A bismuth atom connects to C(8) of this group with a typical Bi−C single bond length of 2.266(5) Å.[51]

In the structure of **6c**, there is one C(7)=C(9) double bond, as well as a new bond between the bismuth atom and the carbon atom. This new carbon skeleton originates from the abstraction of three hydrogens from the former isopropyl substituent. The formation of a Bi—C bond in the product implicates bismuth as the active metal. Limberg et al. attributed Bi(III) C—H activation in their complexes to a proximity-induced effect;[28] a similar effect may be operative in our system. This result strengthens the connection between propene activation in the SOHIO process and the bismuth aryloxide model systems.

B. Ligands with Arene Substituents. In order to explore the possibility of Bi-π-interactions,[30,52,53] we incorporated unsaturated *ortho* substituents onto the aryl rings. The precursor 2,6-diphenylphenol was commercially available, and the 2,6-dibenzylphenol was either purchased or synthesized by base catalyzed aldol condensation, followed by rearrangement (eq 5).[45,54] Both base and acid have been used to catalyze the condensation, but the base catalyzed reaction has better yield. For the bismuth tris(2,6-diphenylphenolate) **9** and tris(2,6-dibenzylphenolate) **10**, the isolated yields were 87% and 88%, respectively. Complex **9** was recently reported by Brym et al. using the metal exchange method, but with lower yield and without elemental analysis.[33]



(5)

The crystal structures of compounds **9** and **10** are shown in Figure 1. In both compounds, three of the phenyl rings form a protective environment about the empty coordination sites on bismuth. The shortest distances between the bismuth centers and the carbons on the substituent phenyl rings are 3.155 Å and 3.083 Å, respectively (Table 2). The shortest reported Bi−C distance for a Bi−arene π-interaction is 3.052 Å,[19,55] while a typical Bi−C covalent bond distance is 2.266(5) Å.[51]

The Bi−arene interactions in compounds **9** and **10** are asymmetric. For bismuth−arene interactions reported in literature (Table 2 and the Schmidbaur review[53]), the distances between bismuth and the centroid of the ring are in the range of 2.96−3.93 Å. The shortest distances between the bismuth centers and the centroids of the phenyl rings in compounds **9** and **10** (3.146 and 3.341 Å, respectively) are inside this range.

B1. Isolation of $Bi_{32}O_4(OH)_4(O\text{-}2,6\text{-}Ph_2C_6H_3)_{12}$ 9c. In the system of $Bi(O\text{-}2,6\text{-}Ph_2C_6H_3)_3$ **9**, an unexpected compound **9c** was obtained during product crystallization (Figure 3). Compound **9c** contains a centrosymmetrical $Bi_{32}O_{56}$ cluster.

Several large bismuth oxide clusters have been reported. Whitmire and co-workers described a series of bismuth clusters obtained using C_6F_5OH as a ligand precursor, of which the largest has a Bi_9O_{20} core.[37] Our group reported bismuth calixarene complexes with Bi_8O_{18} cores.[20,21,24] Mehring recently reported a series of bimetallic sodium bismuth oxo clusters separated from the reaction of $BiCl_3$ and $NaOSiMe_3$, of which the largest is $[Bi_{50}Na_2O_{64}(OH)_2(OSiMe_3)_{22}]\cdot 2C_7H_8\cdot 2H_2O$.[56] The Dikarev group more recently reported a large bismuth oxido diketonate cluster with a $Bi_{38}O_{45}$ core,[57] while the Andrews group reported a bismuth oxido salicylate cluster with a $Bi_{38}O_{44}$ core.[58] The structures of these bismuth oxo clusters can give insight into the mechanism of bismuth oxide formation in solution.[56]

Compound **9c** has a core−shell structure (Figure 3). The metal oxide core consists of fused rings of bismuth and oxygen atoms, while the organic shell is made up of 12 2,6-diphenylbenzene groups. The core and the shell are linked by twelve oxygen atoms. Similar inorganic core−organic shell structures were also found in Whitmire's bismuth phenolate clusters,[37] Mehring's bismuth siloxide clusters,[56] Dikarev's bismuth diketonate clusters,[57] and our bismuth calixarene clusters.[20,21,23,24] In a catalytic system, such an inorganic core with a large number of Bi atoms (32 in compound **9c**) may potentially play the role

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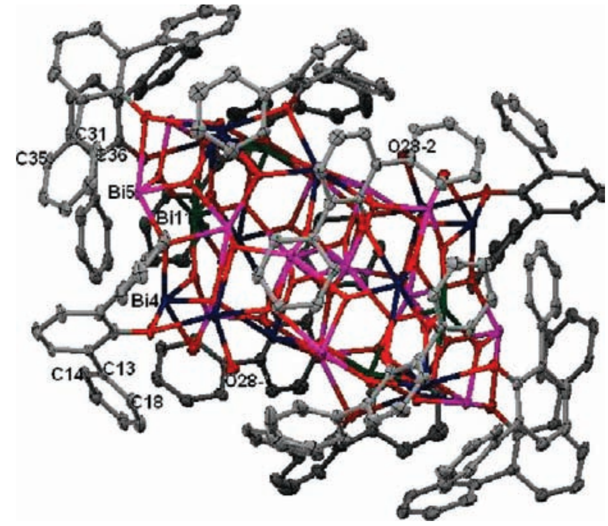

Figure 3. View of the compound **9c**. Bismuth atoms with different coordination numbers are shown in different colors: CN = 3 in yellow, CN = 4 in pink, CN = 5 in blue, CN = 6 in green.

of a solid Bi_2O_3 catalyst, while the organic shell might improve the solubility in organic solvents and/or interactions with organic reagents.

The phenyl rings in the shell have weak asymmetric π-interactions with the bismuth atoms in the core structure. These interactions are similar to those observed in Bi(O-2,6-(benzyl)$_2C_6H_3$)$_3$ **10**, Bi(O-2,6-$Ph_2C_6H_3$)$_3$ **9**, and Bi-($OCPh_3$)$_3$.[19] The average distances between the three closest carbon atoms and the corresponding bismuth atoms range from 3.30 Å (average interaction of Bi(5) with C(31), C(35), and C(36)) to 3.74 Å (average interaction of Bi(4) with C(18), C(13), and C(14)) (Figure 3). They are consistently shorter than the sum of the van der Waals radii (4.00 Å for Bi-aromatic C).[59] The orientations of the phenyl substituents vary over a range from mutually perpendicular to almost parallel. The π-interactions between the bismuth atoms in the core and the phenyl rings in the shell provide a well-protected core when compared to other bismuth oxo clusters with alkoxide or siloxide ligands.[56]

Mehring describes a number of bismuth oxide clusters as based on a $Bi_6O_8^{2+}$ structural unit, combining to build up progressively larger clusters.[56] We can use a similar method to describe our cluster **9c**, but we would find many distortions in the Bi_6 octahedra, as well as many missing O bridges. This difference may be due to the bulkiness of the diphenylphenolate ligand shell.

Instead, we will compare the layers that are formed in the core structure of compound **9c** (see Figure 4) to those of three clusters reported in recent years. These compounds are the [$Bi_{22}O_{26}$($OSiMe_2{}^tBu$)$_{14}$] cluster reported by Mansfeld et al.,[60] the [$Bi_{38}O_{45}$(hfac)$_{24}$] cluster reported by Dikarev et al.,[57] and the [$Bi_{38}O_{44}$(Hsal)$_{26}$-(Me_2CO)$_{16}$(H_2O)$_2$]·4Me_2CO cluster reported by Andrews et al.[58] Despite the differences between the silanolate, hexafluoroacetylacetonate, salicylate, and 2,6-diphenylphenolate ligand environments, the similarities between the four bismuth oxide cores are striking.

For the smaller two clusters (Mansfeld's $Bi_{22}O_{26}$[60] and $Bi_{32}O_{56}$ **9c**), there are three layers, in an A, B, A′ pattern. For the larger clusters (Dikarev's[57] and Andrews'[58] Bi_{38}), there are four layers in an A, B, B′, A′ pattern. The structural similarity throughout all of the clusters is evident, with an interesting addition of a central oxygen chain found only in the Dikarev structure[57] (passing through the center of the cluster, parallel to the bismuth layers).

There is strong similarity between the "A" layers of all four clusters (Figure 5), although distances vary (emphasized by dashed lines for long Bi−O contacts). Characteristic adjoining Bi_4O_4 ladders[21,24,37,47,56] are most clearly seen in the Dikarev A layer[57] and **9c**, while the Andrews and Mansfeld structures include smaller fragments of the similarly patterned layer.

Figure 6 shows the B layers of the four clusters. Again there is structural similarity, especially between the two Bi_{38} clusters.[57,58] The "extra" oxygen may be seen in the center polyhedron of the Dikarev structure.[57] In the case of the B layer, the Bi_{32} cluster **9c** has a more open framework, compared to the ordered array of Bi_3O_4 polyhedra shown in the other B layers. This may be caused by the bulkiness of the diphenylphenolate ligands. In all cases, chains of Bi_2O_2 diamonds are observed, but again, the distances are quite variable.

The bismuth oxygen bonds in the core structure of **9c** have bond lengths varying from 2.056(10) to 2.734(10) Å. The terminal Bi−O bonds (average = 2.537 Å) are significantly longer than the Bi−O bonds in the monomer of compound **4** (average = 2.105 Å). The bismuth atoms in compound **9c** adopt coordination numbers of 3, 4, 5, or 6 (weak Bi−aryl interactions were neglected for all cases). All of the coordination geometries are distorted from the predicted VSEPR structures.

In compound **9c**, most of the bismuth atoms have the coordination number of 4 (Figure 3, in pink). There are 16 of them in total, and they have similar geometries. For instance, Bi(7) is coordinated to O(9), O(10), O(12), and O(13) with all the bond angles less than 109° (79.7(3), 80.3(3), 83.6(4), and 81.9(3)°). It may be interpreted as a distorted trigonal bipyramidal structure with an empty coordination site in the equatorial plane. Two phenyl rings are oriented in favorable positions for π-interactions with the bismuth at the empty coordination site. The O−Bi−O bond angle between the two apical oxygen atoms and the bismuth atom is 155.1(3)°. The equatorial O−Bi−O bond angle is 82.0(6)°, significantly less than 120°. There are no reports of molecular four-coordinated bismuth oxygen complexes, but there are reports of organometallic bismuth complexes with similar distorted trigonal bipyramidal structures.[61]

There are 12 bismuth atoms with the coordination number of 5 in compound **9c** (Figure 3, in blue). We will take Bi(4) as an example to discuss them. Bi(4) adopts a distorted square pyramidal structure with bond angles of 84.0(3), 71.7(3), 102.2(3), and 95.4(3)° in the basal plane. The bond angles between the apical oxygen atom, the bismuth atom, and the four basal oxygen atoms are 87.1(3), 83.1(3), 74.8(3), and 78.5(3)°, respectively. Again, the empty site on the bismuth is well-shielded by phenyl

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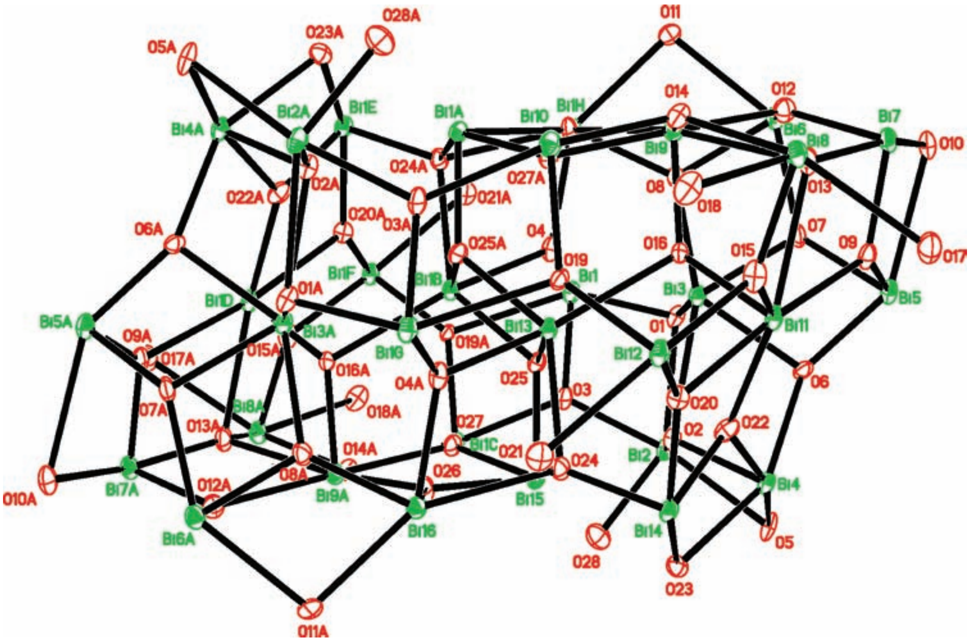
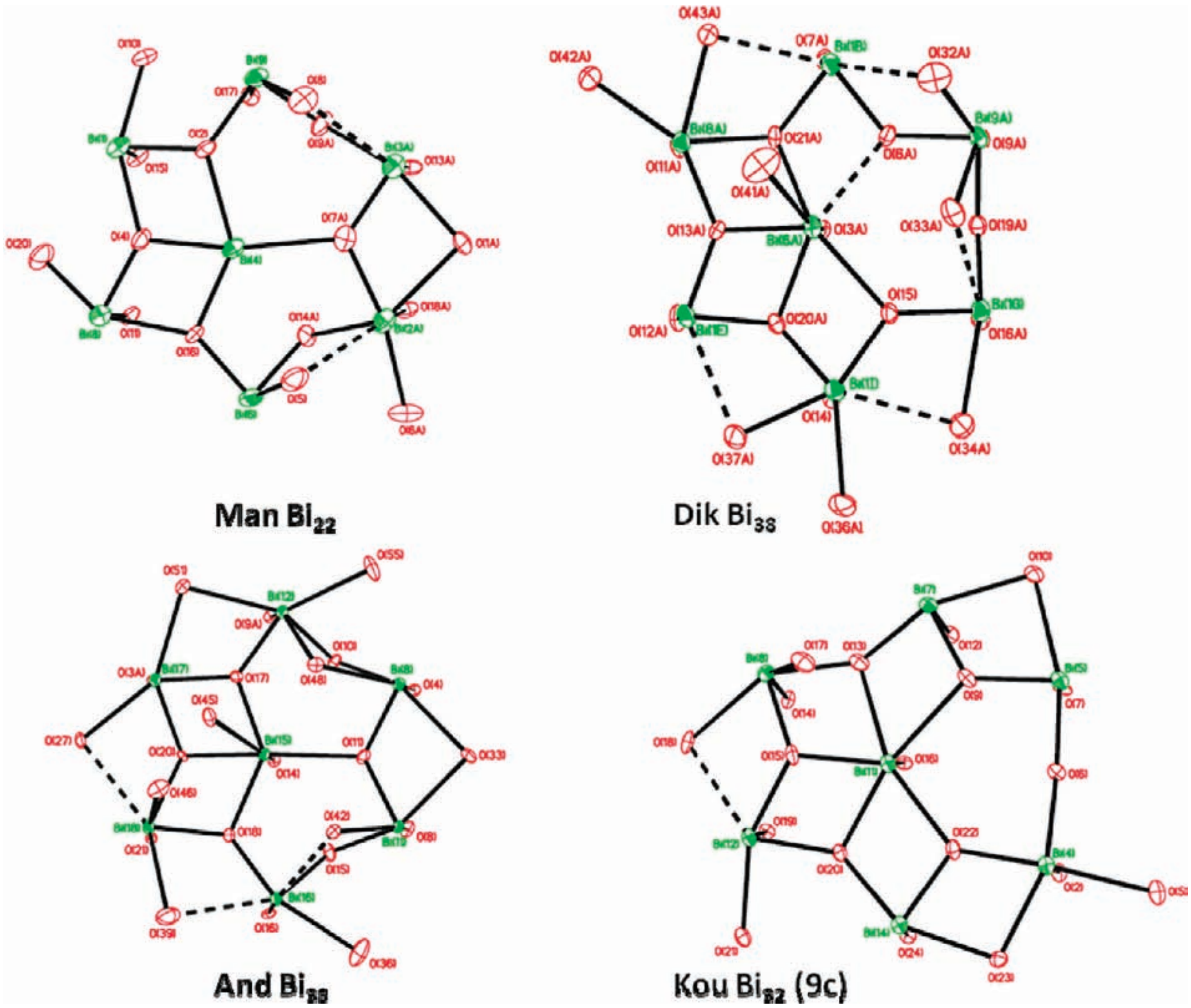


Figure 4. Core structure of compound **9c**.


Man Bi_{22}

Dik Bi_{38}

And Bi_{38}

Kou Bi_{32} (9c)

Figure 5. A layers for clusters $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$,[60] $[Bi_{38}O_{45}(hfac)_{24}]$,[57] $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot 4Me_2CO$,[58] and $Bi_{32}O_4(OH)_4(O\text{-}2,6\text{-}Ph_2C_6H_3)_{12}$ **9c**.

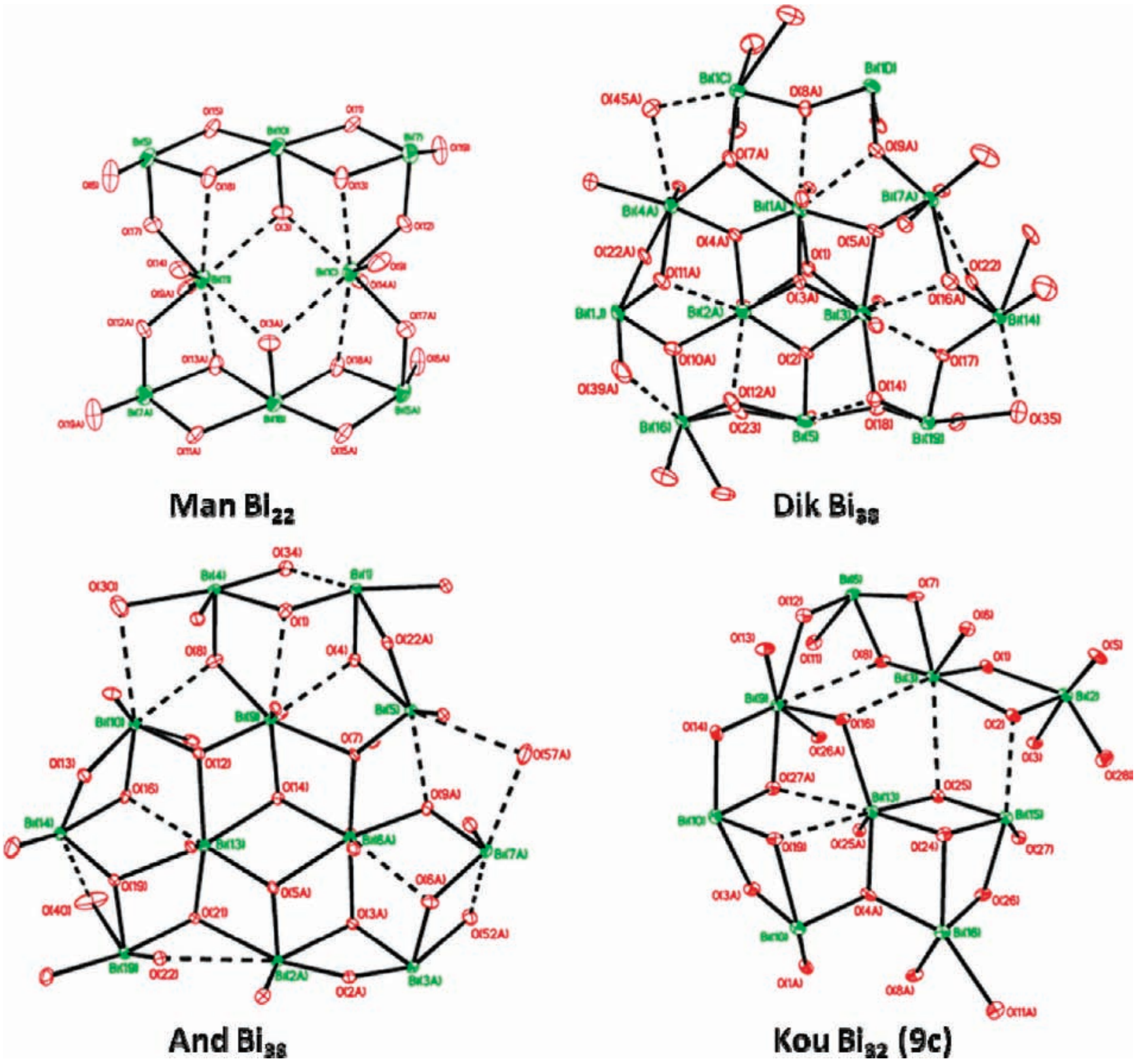


Figure 6. B layers for clusters $[Bi_{22}O_{26}(OSiMe_2{}^tBu)_{14}]$,[60] $[Bi_{38}O_{45}(hfac)_{24}]$,[57] $[Bi_{38}O_{44}(Hsal)_{26}(Me_2CO)_{16}(H_2O)_2]\cdot 4Me_2CO$,[58] and $Bi_{32}O_4(OH)_4(O\text{-}2,6\text{-}Ph_2C_6H_3)_{12}$ **9c**.

rings in the organic shell. In the literature, five-coordinate bismuth−oxygen complexes are generally described as square pyramidal structures or trigonal bipyramidal structures.[37,62,63] Five-coordinate bismuth atoms in α-Bi_2O_3 also have square pyramidal structures.[64]

There are four bismuth atoms with the coordination number of 6 in compound **9c** (Figure 3, in green). For example, in Bi(11), the six oxygen-bound ligands define a distorted pentagonal pyramid with six Bi−O bonds of 2.667(10), 2.654(8), 2.454(10), 2.346(9), 2.213(9), and 2.116(8) Å, respectively. Whitmire defines the coordination environment of the bismuth atoms in $NaBi_4(\mu_3\text{-}OR)_2(OR)_9(THF)_2$ as composed of six oxygen atoms and one lone pair of electrons in a distorted pentagonal bipyramidal array.[37] For Bi(11), the structure may also be described as distorted pentagonal pyramidal, with arene rings shielding the empty coordination site. The O−Bi−O bond angles in the basal plane are 99.2(3), 63.7(3), 68.7(3), 66.6(3), and 66.4(3)°. The bond angles between the apical oxygen atom, the bismuth atom, and the oxygen atoms on the basal plane are 87.7(3), 88.8(3), 89.1(3), 96.2(3), and 72.1(3)°.

Finally, as shown in Figure 4, compound **9c** has unique oxygen atoms O(23) and O(28). The positions of the corresponding H atoms were not found from the F-maps. To provide the correct charge balance for **9c**, an additional four hydrogens should be in the core of the compound. We suggest that the two O atoms (O(23) and O(28)) and their symmetrical equivalents are OH groups, so that the formula of **9c** is $(C_{18}H_{13}O)_{12}Bi_{32}O_{40}(OH)_4$. The positions and structural functions for these two O atoms are different from those for the other O atoms in the $Bi_{32}O_{56}$ core. The O(28) atom is terminal, and the O(23) atom is the only μ^2 bridge between two bismuth atoms in the central core; the other O atoms not bonded to ligands are μ^3 bridges between bismuth atoms.

The Bi(2), a O(28) distance, 2.137(10) Å, is too short for a coordinated H_2O molecule (literature values of 2.61(1)−3.00(1) Å[63]). This distance is slightly shorter than

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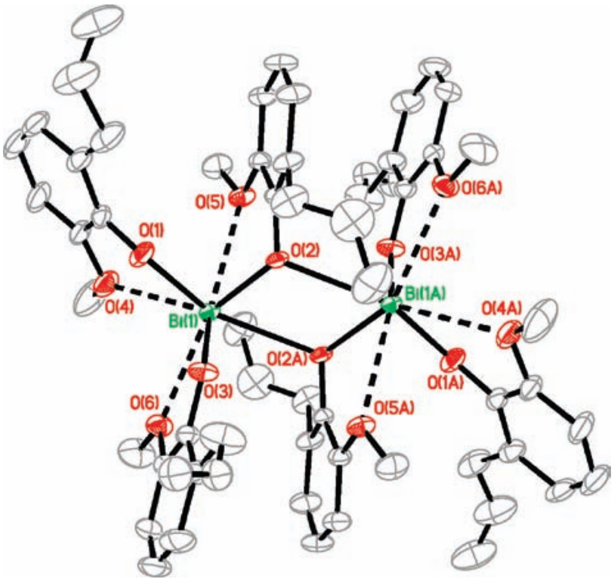

Figure 7. Diagram of the molecular structure of **13**, a bismuth aryloxide with dimer geometry. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms have been omitted for clarity.

that expected for a terminal OH group (literature values of 2.29(1)−2.48(1) Å[63]), but not sufficiently short to consider it a Bi=O double bond (terminal oxo groups have not been reported on bismuth oxo clusters,[65] and a terminal oxo group would also not be consistent with a Bi(III) oxidation state). The bridging Bi(μ^2-OH)Bi group in $[Ar^2Bi(OH)Br]_2$ (Ar^2 = 2,6-Mes_2-4-^{t}BuC_6H_2) contains similar Bi—O distances of 2.553(6) and 2.138(6) Å.[52] The O(23)—Bi(4) and O(23)—Bi(14) distances in Bi(4)—O(23)—Bi(14) μ^2 bridges (2.376(9) and 2.339(9) Å, respectively) are longer than the typical Bi—O distances in Bi(μ^2-O)Bi bridges but close to Bi—O distances (2.390 and 2.485 Å) found for a Bi(μ^2-OH)Bi bridge in $C_{45}H_{141}Bi_{10}Na_5O_{28}Si_{15}\cdot 1.5C_7H_8$.[66]

C. Ligands with Allylic Substituents. The apparent C—H activation process described in section A3 occurred in very small yields, but may be encouraged by the presence of active allylic hydrogens in proximity to the bismuth center. Such ligands may also be viewed as models of the propene substrate that is activated in the SOHIO process.[4] Accordingly, we have synthesized a selection of bismuth aryloxides containing allylic groups in various positions: $Bi[O\text{-}2\text{-}(CH_2CH{=}CH_2)C_6H_4]_3$ **11,** $Bi[O\text{-}2\text{-}(CH{=}CHCH_3)C_6H_4]_3$ **12**, $[Bi[O\text{-}2\text{-}OCH_3\text{-}6\text{-}(CH_2CH{=}CH_2)C_6H_3]_3]_2$ **13**, and $[Bi[O\text{-}2\text{-}OCH_3\text{-}4\text{-}(CH_2CH{=}CH_2)C_6H_3]_3]_2$ **14**, with isolated yields of 73−88%.

We have generally found that the alcohol exchange reaction with $Bi[N(SiMe_3)_2]_3$ (eq 2) is the most convenient method to prepare these bismuth aryloxides (see section A). The starting phenols are commercially available.

Crystal structures of compounds **13** (Figure 7) and **14** (Figure 8) do not show any significant Bi−allyl interactions. Although most of the bismuth aryloxides reported here are monomeric, $Bi(OAr)_3$ **13** is a dimer bridged by phenolate oxygen atoms, and **14** is a polymer chain composed of phenolate-bridged dimers. In complex **14**, two of the methoxy groups chelate to bismuth atoms with Bi−O distances of 2.664(3) and 2.706(3) Å. The third methoxy group bridges to a bismuth atom in the neighboring dimer, with a distance of 2.933(15) Å. In complex **13**, all three methoxy groups have chelating interactions with distances of 2.772(15), 2.766(16), and 2.785(15) Å. Presumably the large allyl groups in the *ortho* positions deter formation of a polymeric chain. The structure of **13** is similar to that of $[Bi(OC_6F_5)_3(tol)_2]_2$ reported by Whitmire et al.[30,55] The Bi−O distances of the phenoxide bridges for compound **13** are 2.167(3) and 2.608(11) Å, and those of compound **14** are 2.183(3) and 2.636(3) Å. They are comparable to Bi−O distances in the Whitmire complex.[30,55]

C1. Isolation of $Li_2Bi_4(\mu^3\text{-}O)_2[O\text{-}2\text{-}(CH_2CH{=}CH_2)C_6H_4]_{10}$ 11c—A Side Product with Lithium Ions. In the reaction of 2-allylphenol and bismuth amide, in addition to the bismuth aryloxide **11**, a side product was obtained from the reaction mixture in low yield (not measured). Complex **11c** was found to be a lithium bismuth oxo cluster $Li_2Bi_4(\mu^3\text{-}O)_2[O\text{-}2\text{-}(CH_2CH{=}CH_2)C_6H_4]_{10}$ (Figure 9). The core geometry is essentially the same as that of $Na_2Bi_4(\mu_3\text{-}O)_2(OC_6F_5)_{10}(THF)_2$, reported by Whitmire et al. in 2000.[37] Mehring recently reported the first metal-oxo cluster containing lithium and bismuth.[67] The Li—O distances in **11c** are 1.915(5) and 2.025(5) Å, which are comparable to Li—O distances in Mehring's complex. The core structure of complex **11c** contains the same Bi_4O_6 subunit as **6c,** a common theme in Bi oxo compounds.[20,21,23−26,37,49] The lithium ion probably comes from LiCl impurity in the bismuth amide starting material. Direct combination of $Bi(OAr)_3$ and LiOAr did not lead to formation of **11c**.

D. Stability of Bismuth Aryloxides. Three stability tests were performed on the 13 bismuth aryloxides (**2**−**14**): shelf life, photolysis, and thermal stability monitored by ^{1}H NMR. All 13 bismuth aryloxides showed no change in their ^{1}H NMR spectra after being in a sealed ampule in their solid form in the glovebox for 1 month. All compounds were also stable to photolysis in CD_3CN solution (monitored by ^{1}H NMR) when irradiated for 10 min, with the exception of $Bi(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}BrC_6H_2)_3$ (**6**), which decomposed to 3,3,'5,5′-tetra-*iso*-propyldiphenoquinone. The same diphenoquinone is obtained upon photolysis of 4-bromo-2,6-diisopropylphenol.

Thermal decomposition in C_6D_6 was studied using ^{1}H NMR. All compounds were stable for up to 3 days at 45 °C. The decomposition temperature of each bismuth aryloxide is shown in Table 3. In all cases the major identifiable product was the corresponding phenol.

$Bi(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}BrC_6H_2)_3$ (**6**) decomposed to the corresponding biphenol byproduct, 3,3′,5,5′-tetra-*iso*-propylbiphenol, as well as phenol when heated at 95 °C for 3 days. The biphenol product is consistent with the formation of phenoxy radical during decomposition.[22] We did not observe deuterium incorporation into phenolic products.

IV. Conclusions

We have described the systematic synthesis and characterization of a large number of bismuth aryloxides. Ring substituents include alkyl, aromatic, allyl, ether, amide, and

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(65) Hoppe, S.; Whitmire, K. H. *Organometallics* **1998**, *17*, 1347–1354.

(66) Mehring, M.; Paalasmaa, S.; Schurmann, M. *Eur. J. Inorg. Chem.* **2005**, 4891–4901.

(67) Mehring, M.; Mansfeld, D.; Costisella, B.; Schurmann, M. *Eur. J. Inorg. Chem.* **2006**, 735–739.

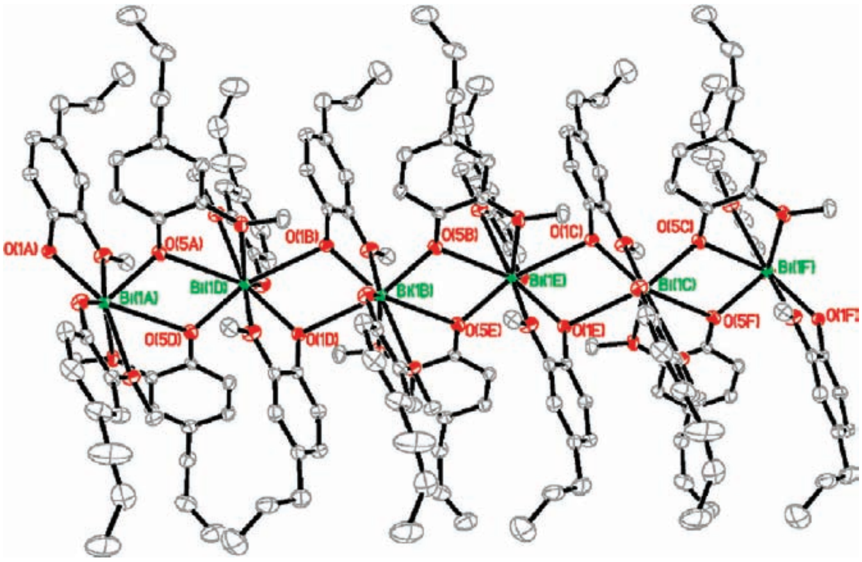

Figure 8. Diagram of the molecular structure of **14**, a bismuth aryloxide with polymer chain geometry. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms have been omitted for clarity.

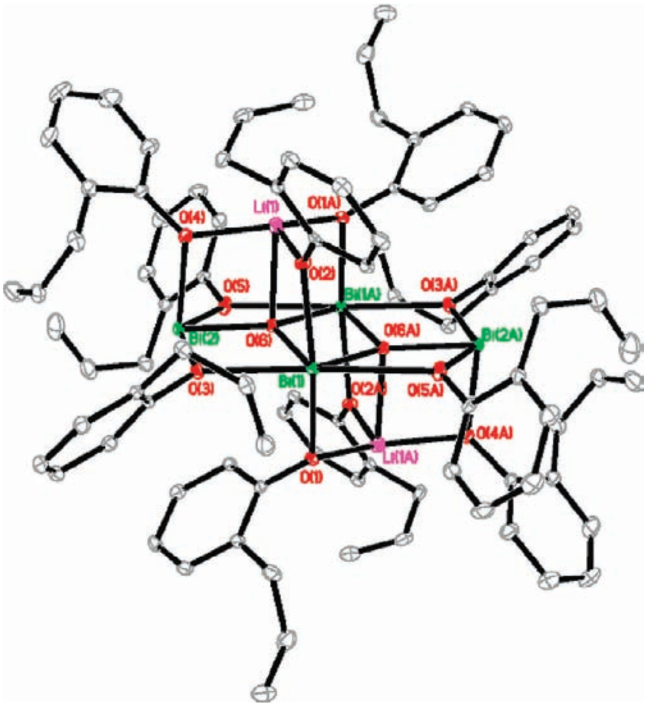

Figure 9. Crystal structure of **11c** (30% probability ellipsoids). H atoms are omitted for clarity.

halogen groups. Their stabilities, spectroscopic, and structural properties were compared. Most $Bi(OAr)_3$ complexes are monomeric, with similar structures about the bismuth centers. These complexes serve as models for oxidation/ammoxidation catalysis,[4] models for bismuth oxide formation by hydrolytic processes,[12] and potential materials precursors.[10,56]

Bi−O bond homolysis of sterically crowded complexes leads to the formation of phenoxy radicals in direct analogy to the Bi−O bond homolysis proposed to intervene in the rate-determining step of the SOHIO oxidation and ammoxidation of propene.[22]

Interesting side products include a Bi−O ladder complex formed by hydrogen abstraction from an ^{i}Pr ligand substituent and a large bismuth oxo cluster presumably formed by microhydrolysis. The characteristic Bi_4O_4 ladder structural motif is seen in several of our clusters. Additionally, it can be seen, from our work and that of others, that bismuth oxide core−shell compounds tend to converge toward very similar inorganic core structures irrespective of the nature of the organic ligand. Others[56] have compared the core structure with that of solid bismuth oxides.

V. Experimental Section

General. All manipulations were performed inside a glovebox under nitrogen atmosphere. 2-*tert*-Butylphenol, 2,6-diphenylphenol, 2-allylphenol, 2-propenylphenol, *o*-eugenol, eugenol, and 2,6-diisopropylphenol were purchased from Aldrich and stored in the glovebox over 3 Å molecular sieves. Bismuth chloride was purchased from Strem and recrystallized from anhydrous ether. $Bi[(N(SiMe_3)_2)]_3$,[35] 2,6-diisopropyl-4-bromophenol,[43] and 2,6-diisopropyl-4-chlorophenol[44] were synthesized as reported in the literature. THF was freshly distilled from Na/benzophenone, and benzene was filtered through activated alumina and Cu-based oxygen absorbent as described by Grubbs et al.[68] Anhydrous pentane and diethyl ether were purchased from Aldrich. All these solvents were stored inside the glovebox over 4 Å molecular sieves for at least 48 h before use. NMR solvents (C_6D_6 and $CDCl_3$) were degassed and dried with CaH_2.

The melting points of the compounds were observed in sealed capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer. IR spectra were obtained with an Infinity Gold FTIR spectrometer. UV/vis spectra were recorded on an Agilent 8453 UV/Visible spectrophotometer. Filtration was done with a medium pore sintered glass frit. The yields reported are from pure isolated products. Elemental analyses were performed by Atlantic Microlabs, Inc.

2,6-Dibenzylphenol was either purchased from Frinton Laboratories, Inc., or synthesized in two steps. 2,6-dibenzylidenecyclohexanone was synthesized by an aldol condensation reaction between cyclohexanone and benzaldehyde.[54] Rearrangement of the isolated product over Pd/C formed 2,6-dibenzylphenol.[69]

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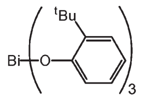
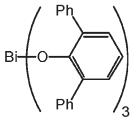
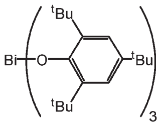
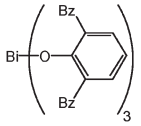
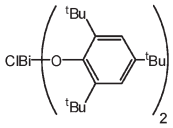
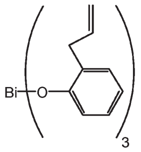
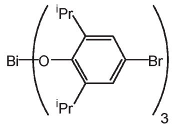
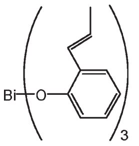
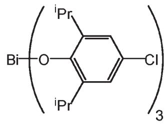
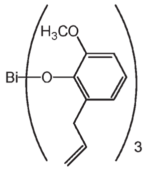
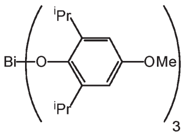
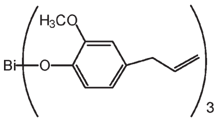
(68) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520.

(69) Horning, E. C. *J. Org. Chem.* **1945**, *10*, 263–265.

Table 3. Decomposition Temperatures of Bismuth Aryloxides in C_6D_6

Cmpd Number	Bi aryloxide	Decomp. Temp. (°C)	Cmpd Number	Bi aryloxide	Decomp. Temp. (°C)
3		95	**9**		stable to 135 °C.
4		75	**10**		135
5		95	**11**		75
6		95[a]	**12**		95
7		95	**13**		135
8		95	**14**		stable to 135 °C.

[a] Decomposition to phenol + 3,3′5,5′-tetra-*iso*-propylbiphenol was observed.

The product was formed in 48% overall yield and was confirmed by comparison of its ^{1}H and ^{13}C NMR spectra with the literature.[70]

2,6-Diisopropyl-4-methoxyphenol was synthesized with a three-step procedure. First, 2,6-diisopropylphenol was oxidized to 2,6-diisopropyl-*p*-benzoquinone with PbO_2.[45] Second, 2,6-diisopropyl-*p*-benzoquinone was reduced to 2,6-bis(1-methylethyl)-1,4-benzenediol with Zn powder.[46] Third, 2,6-bis(1-methylethyl)-1,4-benzenediol was methylated with dimethyl sulfate under basic conditions.[71] The overall yield is 20% and the product was confirmed by comparison of its ^{1}H and ^{13}C NMR spectra with the literature.[71]

Photolysis was performed using in a Rayonet photochemical reactor manufactured by The Southern New England Ultraviolet Company. A 10 mg portion of each $Bi(OAr)_3$ was placed in a quartz NMR tube, and 0.6 mL CD_3CN was added. The tube was placed in the photochemical reactor for 10 min. All compounds showed no change in the NMR spectrum with the exception of $Bi(O\text{-}2,6\text{-}^iPr_2\text{-}4\text{-}BrC_6H_2)_3$ (**6**).

Solution decomposition of each compound was studied using ^{1}H NMR spectroscopy. A 10 mg portion of each $Bi(OAr)_3$ was sealed under vacuum in an NMR tube with 0.6 mL C_6D_6. The sample was then left at room temperature for 3 days, then heated in an isotemp oil bath to 45, 75, 95 and 135 °C for 3 days each. Once decomposition occurred, the sample was no longer heated.

All compounds were stable when placed in a glass ampule, sealed under vacuum, and placed in the glovebox for 1 month.

$Bi(O\text{-}2,6\text{-}^iPr_2C_6H_3)_3$ (2). A solution of 2,6-diisopropylphenol (1.05 g, 5.93 mmol) in 10 mL of THF was added to a solution of $Bi[(N(SiMe_3)_2)]_3$ (1.37 g, 1.98 mmol) in 10 mL of THF. The yellow solution was stirred overnight. The solvent was then removed under vacuum to obtain yellow powder, which was dissolved in pentane. The solution was filtered and kept at −35 °C to produce a yellow precipitate. The supernatant was decanted and the solid dried in vacuo to produce 1.015 g of **2** (69% yield). Yellow rod crystals (0.30 × 0.08 × 0.08 mm^3) of **2** were obtained at −35 °C from a concentrated THF solution for X-ray analysis. mp: 165−166 °C (melt and dec). ^{1}H NMR (C_6D_6): δ (ppm) 7.05 (d, 6H, J = 8 Hz, Ar*H*), 6.63 (t, 3H, J = 8 Hz, Ar*H*), 3.69 (septet, 6H, J = 7 Hz, C*H*Me$_2$), 1.12 (d, 36H, J = 7 Hz, C*H*$_3$). ^{13}C NMR (C_6D_6): δ (ppm) 154.4 (*C*-OBi), 141.2, 122.8 (aromatic), 121.9 ($C\text{-}^iPr$), 27.7 ($CH(CH_3)_2$), 24.8 ($CH(CH_3)_2$). IR (C_6H_6): 3086, 3007, 1974, 1945, 1801, 1474, 1422, 1318, 1179, 865, 758, 684, 659 cm^{-1}. UV/vis (C_6H_6) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 349 (7000). Elemental analysis gave unsatisfactory results, so a high resolution mass spectrum was obtained. HRMS (CI) *m*/*e* calcd for $C_{36}H_{51}O_3Bi$: 740.3642 (M$^+$). Found: 740.3647 (M$^+$).

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(70) Mukawa, T.; Inoue, Y.; Shiraishi, S. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2549–2556.

(71) Petranek, J.; Pilar, J. *Collect. Czech. Chem. Commun.* **1970**, *35*, 830–837.

Thermolysis of Bi(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$ (2). An 11 mg portion of Bi(O-2,6-^{i}Pr$_2$C$_6$H$_3$)$_3$ (0.015 mmol) and 8 mg of Ph$_3$CH (0.033 mmol, as internal standard) were dissolved in 2 mL C$_6$D$_6$, and a yellow solution was obtained. The yellow solution was added to an NMR tube, and then, the tube was sealed under vacuum. The tube was left in the 135 °C oil bath for 1 week. The weight percentage of the decomposition products was calculated by the comparison of the integration of the peaks in ^{1}H NMR. The authentic sample of diphenoquinone was synthesized by the oxidation of the 2,6-diisopropylphenol with PbO$_2$ in acetic acid, and the biphenol (3,3′,5,5′-tetra-*iso*-propylbiphenol) was obtained by the reduction of the diphenoquinone with Na$_2$S$_2$O$_4$ in ethanol.[46]

Bi(O-2-^{t}BuC$_6$H$_4$)$_3$ (3). A solution of 2-*tert*-butylphenol (0.45 g, 3.0 mmol) in 10 mL of pentane was added to a solution of Bi[(N(SiMe$_3$)$_2$)]$_3$ (0.69 g, 1.0 mmol) in 10 mL of pentane. The yellow solution obtained was allowed to stir overnight. Solvent was then removed under vacuum, and the solid produced was washed with pentane (2 × 3 mL) and dried under vacuum to obtain a yellow solid (0.55 g, 84% yield). mp: 125 °C (dec). ^{1}H NMR (C$_6$D$_6$): δ (ppm) 7.52 (d, 3H, J = 8 Hz, Ar*H*), 7.05 (t, 3H, J = 8 Hz, Ar*H*), 6.95 (d, 3H, J = 8 Hz, Ar*H*), 6.83 (t, 3H, J = 8 Hz, Ar*H*), 1.54 (s, 27H, ^{t}Bu). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 158.1 (*C*-O), 142.2 (*C*-^{t}Bu), 127.7, 128.8, 121.1, 119.8 (aromatic carbons), 34.9 (*C*(CH$_3$)$_3$), 30.3 (C(*C*H$_3$)$_3$). IR (C$_6$H$_6$): 3072, 3044, 1959, 1815, 1478, 1437, 1213, 1035, 664, 460 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 277 (2104), 322 (703). Anal. calcd. for BiO$_3$C$_{30}$H$_{39}$: C, 54.88; H, 5.99. Found: C, 54.72; H, 6.00. Compound **3** was stable after heating for 3 days at 75 °C. When heated at 95 °C for 3 days, most of the compound had decomposed to the corresponding phenol. Additional heating at 135 °C for 3 days showed only a small increase in phenol. The remaining bismuth product continued to be stable with no change in the NMR when the NMR tube was exposed to air for 5 min. After 12 h, the NMR showed only the phenol product.

Bi(O-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_3$ (4). A suspension of the lithium salt of 2,4,6-tri-*tert*-butylphenol (0.130 g, 0.484 mmol) in 5 mL of pentane was added to a suspension of BiCl$_3$ (0.079 g, 0.25 mmol) in 2 mL of pentane. The green suspension was stirred for 1 h. The black precipitate was then filtered out, and the green solution was put into the freezer. After 12 h, a yellow solid formed on the bottom of vial. The precipitate was filtered out and washed with cold pentane (2 × 2 mL) and dried under vacuum to obtain a yellow powder (0.12 g, 25% yield). mp: 123−124 °C (dec). ^{1}H NMR (C$_6$D$_6$): δ (ppm) 7.42 (s, 6H, Ar*H*), 1.49 (s, 54H, *ortho*-^{t}Bu), 1.35 (s, 27H, *para*-^{t}Bu). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 153.8 (*C*-OBi), 143.0 (*C*-^{t}Bu), 141.7 (*C*-^{t}Bu), 123.3 (aromatic), 36.1 (*ortho*-*C*(CH$_3$)$_3$), 34.2 (*para*-*C*(CH$_3$)$_3$), 34.1 (*ortho*-C(*C*H$_3$)$_3$), 32.3 (*para*-C(*C*H$_3$)$_3$). IR (C$_6$H$_6$): 3079, 3025, 2946, 2876, 2856, 1492, 1402, 1200, 1176, 1094, 697, 644 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 278 (6000), 379 (2420). The product was not sufficiently stable to submit for elemental analysis. Complete decomposition of compound **4** to the corresponding phenol occurred after the solution was heated for 3 days at 75 °C.

ClBi(O-2,4,6-^{t}Bu$_3$C$_6$H$_2$)$_2$ (5). A suspension of the lithium salt of 2,4,6-tri-*tert*-butylphenol (0.069 g, 0.26 mmol) in 5 mL of pentane was added to a suspension of BiCl$_3$ (0.079 g, 0.25 mmol) in 2 mL of pentane. The dark green suspension was stirred overnight. The black precipitate was then filtered out, and the dark green solution was put into the −35 °C freezer. After 12 h, red solid formed on the bottom of vial. The precipitate was filtered out, washed with cold pentane (2 × 2 mL), and dried under vacuum to obtain a red powder (0.040 g, 0.052 mmol, 40% yield). Red platelet crystals (0.52 × 0.20 × 0.09 mm^3) of **4** were obtained at −35 °C from a concentrated pentane solution for X-ray analysis. mp: 146−147 °C. ^{1}H NMR (C$_6$D$_6$): δ (ppm) 7.62 (s, 4H, Ar*H*), 1.65 (s, 32H, *ortho*-^{t}Bu), 1.39 (s, 18H, *para*-^{t}Bu). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 144.0 (*C*-OBi), 143.5 (*C*-^{t}Bu), 128.8 (*C*-^{t}Bu), 121.7 (aromatic), 35.6 (*ortho*-*C*(CH$_3$)$_3$), 34.2 (*para*-*C*(CH$_3$)$_3$), 34.0 (*ortho*-C(*C*H$_3$)$_3$), 32.5 (*para*-C(*C*H$_3$)$_3$). IR (C$_6$H$_6$): 3624, 3066, 2953, 2863, 1531, 1495, 1252, 1085, 1061, 998, 799, 687, 631 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 285 (4890), 397 (2000). Anal. calcd. for BiO$_2$C$_{36}$H$_{58}$Cl: C, 56.35; H, 7.62. Found: C, 56.27; H, 7.57. Compound **5** was stable at 75 °C in C$_6$D$_6$ solution for 3 days. Decomposition to the corresponding phenol occurred after heating the solution to 95 °C for 3 days.

Bi(O-2,6-^{i}Pr$_2$-4-BrC$_6$H$_2$)$_3$ (6). A solution of 2,6-diisopropyl-4-bromophenol (0.39 g, 1.5 mmol) in 10 mL of pentane was added to a solution of Bi[(N(SiMe$_3$)$_2$)]$_3$ (0.35 g, 0.51 mmol) in 5 mL of pentane. Yellow precipitate was formed after 4 h. The suspension was stirred for another 8 h. The precipitate was filtered out and washed with pentane (2 × 2 mL) and dried under vacuum to obtain a yellow powder (0.33 g, 68% yield). Yellow block crystals (0.54 × 0.46 × 0.28 mm^3) of **6** were obtained at −35 °C from a concentrated pentane solution for X-ray analysis. mp: 130 − 132 °C (melt and dec). ^{1}H NMR (C$_6$D$_6$): δ (ppm) 7.39 (s, 6H, Ar*H*), 3.17 (septet, 6H, J = 7 Hz, C*H*Me$_2$), 1.00 (d, 36H, J = 7 Hz, Me). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 151.1 (*C*-OBi), 143.0 (*C*-Br), 126.0 (aromatic), 116.3 (*C*-^{i}Pr), 27.8 (*C*H(CH$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$). IR (C$_6$H$_6$): 3083, 3036, 2960, 1963, 1824, 1483, 1422, 1318, 1258, 1179, 1094, 803, 712, 678 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 277 (1497), 345 (395). Anal. calcd. for BiO$_3$C$_{36}$H$_{48}$Br$_3$: C, 44.24; H, 4.95. Found: C, 44.48; H, 5.06. Compound **6** was stable at 75 °C in C$_6$D$_6$ solution for 3 days. Decomposition to phenol and 3,3′,5,5′-tetra-*iso*-propylbiphenol (approximately 9:1 ratio) occurred after heating the solution to 95 °C for 3 days. The biphenol was identified by comparison to an authentic sample.[46]

By slow evaporation of the filtrate solution at −35 °C, light yellow block crystals (0.30 × 0.20 × 0.10 mm^3) with the bismuth oxide cluster structure (**6c**) were obtained twice; however, the yield is quite low (not measured, < 5%).

Bi(O-2,6-^{i}Pr$_2$-4-ClC$_6$H$_2$)$_3$ (7). A solution of 2,6-diisopropyl-4-chlorophenol (0.32 g, 1.5 mmol) in 10 mL of hexane was added to a solution of Bi[(N(SiMe$_3$)$_2$)]$_3$ (0.35 g, 0.51 mmol) in 5 mL of hexane. Yellow precipitate formed after 4 h. The suspension was stirred for another 8 h. The precipitate was filtered out and washed with pentane (2 × 2 mL) and dried under vacuum to obtain yellow powder (0.23 g, 55% yield). Yellow prismatic crystals (0.28 × 0.17 × 0.13 mm^3) of **7** were obtained at −35 °C from a concentrated ether solution for X-ray analysis. mp: 163 − 165 °C (melt and dec). ^{1}H NMR (C$_6$D$_6$): δ (ppm) 7.24 (s, 6H, Ar*H*), 3.19 (septet, 6H, J = 6 Hz, C*H*Me$_2$), 1.02 (d, J = 6 Hz, 36H, C*H*$_3$). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 150.7 (*C*-OBi), 142.6 (*C*-^{i}Pr), 126.0 (overlapping *C*-Cl and aromatic), 28.0 (*C*H(CH$_3$)$_2$), 23.8 (CH(*C*H$_3$)$_2$). IR (C$_6$H$_6$): 3086, 3007, 1974, 1945, 1801, 1474, 1422, 1318, 1179, 865, 758, 684, 659 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 281(4466). Anal. calcd. for BiO$_3$C$_{36}$H$_{48}$Cl$_3$: C, 51.22; H, 5.73. Found: C, 50.73; H, 5.79. Compound **7** was stable after heating for 3 days at 75 °C. Decomposition to the corresponding phenol occurred at 95 °C.

Bi[O-2,6-^{i}Pr$_2$-4-(OCH$_3$)C$_6$H$_2$]$_3$ (8). A solution of 2,6-diisopropyl-4-methoxyphenol (0.31 g, 1.5 mmol) in 10 mL of hexane was added to a solution of Bi[(N(SiMe$_3$)$_2$)]$_3$ (0.35 g, 0.51 mmol) in 5 mL of hexane. The yellow solution was stirred for 1 day. Yellow precipitate formed. The precipitate was filtered out, washed with pentane (2 × 2 mL), and dried under vacuum to obtain yellow powder (0.19 g, 45% yield). mp: 65−69 °C (melt and dec). ^{1}H NMR (C$_6$D$_6$): δ (ppm) 6.89 (s, 6H, Ar*H*), 3.51 (septet, 6H, J = 7 Hz, C*H*Me$_2$), 3.51 (s, 9H, OC*H*$_3$), 1.25 (d, 36H, J = 7 Hz, CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ (ppm) 141.6 (*C*-OBi), 127.2 (*C*-CH$_3$), 126.9 (aromatic), 108.5 (*C*-^{i}Pr), 55.1 (O*C*H$_3$), 27.9 (*C*H(CH$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$). IR (C$_6$H$_6$): 3086, 3007, 1974, 1945, 1801, 1474, 1422, 1318, 1179, 865, 758, 684, 659 cm^{-1}. UV/vis (C$_6$H$_6$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 284 (4045). Anal. calcd. for BiO$_6$C$_{39}$H$_{57}$: C, 56.38; H, 6.92.

Found: C, 56.35; H, 7.15. Compound **8** was stable after heating for 3 days at 75 °C. Decomposition to the corresponding phenol occurred at 95 °C.

$\mathbf{Bi[O\text{-}2,6\text{-}(C_6H_5)_2C_6H_3]_3}$ (9). A solution of 2,6-diphenylphenol (0.37 g, 1.5 mmol) in 10 mL ether was added to a solvent bomb (vacuum schlenck tube) containing a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.35 g, 0.51 mmol) in 10 mL ether. The yellow solution was heated at 45 °C in an oil bath for 12 h. When the solution was cooled down to room temperature, yellow cubic shaped crystals were obtained and filtered out (0.41 g, 87% yield). Yellow block crystals ($0.30 \times 0.20 \times 0.10$ mm^3) of **9** were obtained by slowly cooling down a concentrated ether solution from 45 °C to room temperature for X-ray analysis. mp: 133 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 6.71 (t, 3H, J = 8 Hz, *para* to O), 6.90−7.37 (m, 36H, Ar*H*). ^{13}C NMR ($\mathrm{C_6D_6}$): δ (ppm) 138.1, 130.2, 129.6, 129.2, 128.9, 120.9 (aromatic carbons, some quaternary carbons were not observed). IR ($\mathrm{C_6H_6}$): 3071, 3044, 1957, 1810, 1480, 1035, 664, 460 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 295 (2447). Anal. calcd. for $\mathrm{BiO_3C_{54}H_{39}}$: C, 68.64; H, 4.16. Found: C, 68.22; H, 3.81. Compound **9** was stable after heating for 3 days at 135 °C. Decomposition to the corresponding phenol occurred when the NMR tube was exposed to air for 5 min.

The filtrate ether solution was put into the −35 °C freezer, and after 2 weeks, light yellow block crystals ($0.17 \times 0.06 \times 0.05$ mm^3) of **9c** were obtained.

$\mathbf{Bi[O\text{-}2,6\text{-}(CH_2C_6H_5)_2C_6H_3]_3}$ (10). A solution of 2,6-dibenzylphenol (0.41 g, 1.5 mmol) in 10 mL ether was added to a solvent bomb containing a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.35 g, 0.51 mmol) in 10 mL ether. The yellow solution was heated at 45 °C in an oil bath for 12 h, then solvent was removed under vacuum to obtain yellow solid. The yellow solid was dissolved in ether and put into a −33 °C freezer for recrystallization; yellow cubic crystals were obtained. The supernatant was decanted and the crystals were dried under vacuum (0.45 g, 88% yield). Yellow needle crystals ($0.15 \times 0.10 \times 0.08$ mm^3) of **10** were obtained at −35 °C from a concentrated ether solution for X-ray analysis. mp: 152−154 °C (dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 6.92−7.16 (m, 36H, Ar*H*), 6.61 (t, 3H, J = 8 Hz, *para* to O), 4.11 (s, 12H, $\mathit{CH_2}\mathrm{Ph}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ (ppm) 155.3 (*C*-O), 142.5 (quat), 133.3, 129.3, 128.91, 128.88, 126.4 (aromatic), 122.0 (*ortho* to O), 37.2 ($\mathit{C}\mathrm{H_2Ph}$). IR ($\mathrm{C_6H_6}$): 3071, 3044, 1958, 1816, 1479, 1036, 663, 459 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 277 (1596). Anal. calcd. for $\mathrm{BiO_3C_{60}H_{51}}$: C, 70.03; H, 5.00. Found: C, 69.75; H, 5.06. Compound **10** was stable after heating for 3 days at 95 °C. Decomposition to the corresponding phenol occurred after heating the solution to 135 °C for 3 days.

$\mathbf{Bi[O\text{-}2\text{-}(CH_2CH{=}CH_2)C_6H_4]_3}$ (11). A solution of 2-allylphenol (0.40 g, 3.0 mmol) in 10 mL of ether was added to a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.69 g, 1.0 mmol) in 5 mL of ether. Yellow precipitate formed at once. After stirring for 4 h, the precipitate was filtered out, washed with pentane (2×3 mL), and dried under vacuum to obtain yellow powder (0.48 g, 80% yield). mp: 110−113 °C (melt and dec). ^{1}H NMR ($\mathrm{CDCl_3}$): δ (ppm) 7.07 (d, 3H, J = 7 Hz, Ar*H*), 6.95 (t, 3H, J = 7 Hz, Ar*H*), 6.69 (t, 3H, J = 7 Hz, Ar*H*), 6.56 (d, 3H, J = 7 Hz, Ar*H*), 5.77 (m, 3H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$), 4.82 (d, 3H, J = 10 Hz, $\mathrm{CH_2CH{=}C}\mathit{H_2}$), 4.67 (d, 3H, J = 17 Hz, $\mathrm{CH_2CH{=}C}\mathit{H_2}$), 3.20 (d, 6H, J = 6 Hz, $\mathrm{C}\mathit{H_2}\mathrm{CH{=}CH_2}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ (ppm) 141.1 (*C*-O), 132.1 (*C*-allyl), 130.2, 127.2, 122.1, 121.8 (aromatic), 116.0 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}CH_2}$), 77.4 ($\mathrm{CH_2CH{=}}\mathit{C}\mathrm{H_2}$), 34.7 ($\mathit{C}\mathrm{H_2CH{=}CH_2}$). IR ($\mathrm{C_6H_6}$): 3075, 3024, 1956, 1817, 1486, 1226, 1034, 664, 459 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 278 (1230). Anal. calcd. for $\mathrm{BiO_3C_{27}H_{27}}$: C, 53.30; H, 4.47. Found: C, 53.04; H, 4.75. Compound **11** was stable after heating for 3 days at 45 °C. Decomposition to the corresponding phenol occurred after heating the solution to 75 °C for 3 days.

Yellow block crystals ($0.25 \times 0.25 \times 0.20$ mm^3) were obtained by slow evaporation of the filtrate pentane solution and found to be a lithium bismuth oxo cluster, **11c**. The yield of the cluster is quite low (not measured, < 5%), and its crystallization was not repeated. The compound was not isolated from the controlled addition of lithium aryloxide to **11**.

$\mathbf{Bi[O\text{-}2\text{-}(CH{=}CHCH_3)C_6H_4]_3}$ (12). A solution of 2-propenylphenol (0.40 g, 3.0 mmol) in 10 mL of ether was added to a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.69 g, 1.0 mmol) in 5 mL of ether. Yellow precipitate formed after 30 min. After stirring overnight, the precipitate was filtered out, washed with pentane (2×3 mL), and dried under vacuum to obtain yellow powder (0.54 g, 88% yield). m.p.: 113−116 °C (melt and dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 7.50 (d, 3H, J = 8 Hz, Ar*H*), 7.07−6.95 (m, 6H, Ar*H* and one allyl proton overlapped), 6.77 (t, 6H, J = 7 Hz, Ar*H*), 6.01 (m, 3H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CH_3}$), 1.82 (d, 9H, J = 6 Hz, $\mathrm{CH{=}CHC}\mathit{H_3}$). ^{13}C NMR ($\mathrm{CDCl_3}$): δ (ppm) 129.1, 127.7, 127.3, 126.7 (aromatic carbons, quarternary carbons were not observed), 122.4 ($\mathit{C}\mathrm{H{=}CHCH_3}$), 121.7 ($\mathrm{CH{=}}\mathit{C}\mathrm{HCH_3}$), 18.8 ($\mathit{C}\mathrm{H_3}$). IR ($\mathrm{C_6H_6}$): 3072, 3028, 1953, 1810, 1478, 1223, 1034, 689, 459 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 292 (1766). Anal. calcd. for $\mathrm{BiO_3C_{27}H_{27}}$: C, 53.30; H, 4.47. Found: C, 53.39; H, 4.57. Compound **12** was stable after heating for 3 days at 75 °C. Decomposition to the corresponding phenol occurred after heating the solution to 95 °C for 3 days.

$\mathbf{Bi[O\text{-}2\text{-}OCH_3\text{-}6\text{-}(CH_2CH{=}CH_2)C_6H_3]_3}$ (13). A solution of *o*-eugenol (0.25 g, 1.5 mmol) in 10 mL of pentane was added to a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.35 g, 0.51 mmol) in 5 mL of pentane. Yellow precipitate formed immediately. After stirring for 5 h, the precipitate was filtered out and dried under vacuum to obtain yellow powder (0.2560 g, 73% yield). Yellow needle crystals ($0.26 \times 0.18 \times 0.13$ mm^3) of **13** were obtained from the reaction mixture in pentane for X-ray analysis. mp: 131 − 134 °C (melt and dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 6.94 (d, 3H, J = 8 Hz, Ar*H*), 6.55 (t, 3H, J = 8 Hz, Ar*H*), 6.25 (d, 3H, J = 8 Hz, Ar*H*), 6.19−6.10 (m, 3H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$), 5.18 (dd, 3H, J_1 = 2 Hz, J_2 = 9 Hz, $\mathrm{CH_2CH{=}C}\mathit{H_2}$), 5.06 (dd, 3H, J_1 = 2 Hz, J_2 = 6 Hz, $\mathrm{CH_2CH{=}C}\mathit{H_2}$), 3.51 (d, 6H, J = 7 Hz, $\mathrm{C}\mathit{H_2}\mathrm{CH{=}CH_2}$), 3.09 (s, 9H, $\mathrm{OC}\mathit{H_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ (ppm) 149.6 (*C*-OBi), 148.5 ($\mathit{C}\mathrm{\text{-}OCH_3}$), 138.8 (aromatic), 133.3 (*C*-allyl), 123.0 (aromatic), 117.7 (aromatic), 114.6 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}CH_2}$), 108.7 ($\mathrm{CH_2CH{=}}\mathit{C}\mathrm{H_2}$), 34.9 ($\mathit{C}\mathrm{H_2CH{=}CH_2}$), 54.9 ($\mathrm{O}\mathit{C}\mathrm{H_3}$). IR ($\mathrm{C_6H_6}$): 3075, 3028, 1957, 1816, 1479, 1273, 1036, 663, 460 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 281 (1415). Anal. calcd. for $\mathrm{BiO_6C_{30}H_{33}}$: C, 51.58; H, 4.76. Found: C, 51.29; H, 4.78. Compound **13** was stable after heating for 3 days at 95 °C. Decomposition to the corresponding phenol occurred after heating the solution to 135 °C for 3 days.

$\mathbf{Bi[O\text{-}2\text{-}OCH_3\text{-}4\text{-}(CH_2CH{=}CH_2)C_6H_3]_3}$ (14). A solution of eugenol (0.25 g, 1.5 mmol) in 10 mL of pentane was added to a solution of $\mathrm{Bi[(N(SiMe_3)_2)]_3}$ (0.35 g, 0.51 mmol) in 5 mL of pentane without stirring. The solution became cloudy at once then became clear again after 30 min. After 1 day undisturbed, needle-shaped crystals formed. These were filtered out and dried under vacuum to obtain light yellow solid (0.26 g, 73% yield). Yellow block crystals ($0.30 \times 0.20 \times 0.10$ mm^3) of **14** were obtained at −35 °C from a concentrated ether solution for X-ray analysis. mp: 131−133 °C (melt and dec). ^{1}H NMR ($\mathrm{C_6D_6}$): δ (ppm) 7.04 (d, 3H, J = 8 Hz, Ar*H*), 6.70 (d, 3H, J = 8 Hz, Ar*H*), 6.35 (s, Ar*H*), 5.98−5.84 (m, 3H, $\mathrm{CH_2C}\mathit{H}\mathrm{{=}CH_2}$), 5.06−5.00 (m, 6H, $\mathrm{CH_2CH{=}C}\mathit{H_2}$), 3.25 (d, 6H, $\mathrm{C}\mathit{H_2}\mathrm{CH{=}CH_2}$), 3.38 (s, 9H, $\mathrm{OC}\mathit{H_3}$). ^{13}C NMR ($\mathrm{C_6D_6}$): δ (ppm) 150.7 (*C*-OBi), 148.9 ($\mathit{C}\mathrm{\text{-}OCH_3}$), 138.8 (*C*-allyl), 129.5, 121.8, 121.6 (aromatic), 114.8 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}CH_2}$), 110.9 ($\mathrm{CH_2CH{=}}\mathit{C}\mathrm{H_2}$), 40.0 ($\mathit{C}\mathrm{H_2CH{=}CH_2}$), 55.1 ($\mathrm{O}\mathit{C}\mathrm{H_3}$). IR ($\mathrm{C_6H_6}$): 3071, 3043, 1956, 1808, 1496, 1261, 664, 459 cm^{-1}. UV/vis ($\mathrm{C_6H_6}$) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 288 (1605). Anal. calcd. for $\mathrm{BiO_6C_{30}H_{33}}$: C, 51.58; H, 4.76. Found: C, 51.74; H, 4.70. Compound **14** was stable after heating for 3 days at 135 °C. Decomposition to the corresponding phenol occurred when the NMR tube was exposed to air for 5 min.

Table 4. Crystallographic Data and Summary of Data Collection and Structure Refinement

compunds	**2**	**5**	**6**	**7**	**9**
formula	$C_{36}H_{51}BiO_3$	$C_{36}H_{58}BiClO_2$	$C_{36}H_{48}BiBr_3O_3$	$C_{36}H_{48}BiCl_3O_3$	$C_{54}H_{39}BiO_3$
fw	740.75	767.25	977.45	844.07	944.83
crystal syst	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	P-1	P-1	P-1	$P2_1/n$
T, K	203(2)	213(2)	213(2)	213(2)	213(2)
a, Å	11.545(3)	9.6368(5)	9.371(4)	9.344(2)	13.0039(6)
b, Å	28.528(6)	13.9896(8)	10.783(5)	10.755(3)	18.9566(9)
c, Å	10.836(2)	14.2872(8)	18.755(9)	18.738(4)	16.4856(8)
α, deg	90.00	78.5150(10)	86.072(7)	86.328(4)	90
β, deg	108.751(3)	85.6060(10)	80.293(7)	79.338(4)	101.0720(10)
γ, deg	90.00	72.4230(10)	81.010(7)	80.079(4)	90
V, Å^3	3379.5(13)	1798.81(17)	1843.2(14)	1821.9(7)	3988.2(3)
Z	4	2	2	2	4
d_{calcd}, mg·m^{-3}	1.456	1.417	1.761	1.539	1.574
μ, mm^{-1}	5.249	5.003	8.066	5.091	4.467
θ range (deg)	1.99–27.00	1.55–22.50	1.91–22.50	2.71–23.27	1.65–28.20
N measd	37349	10587	10692	10543	28608
N ind	7318 [R(int) = 0.0261]	4714[R(int) = 0.0810]	4808 [R(int) = 0.1632]	4755 [R(int) = 0.0448]	9339 [R(int) = 0.0288]
R_1	0.0198	0.0309	0.0565	0.0225	0.0234
ωR_2	0.0476	0.0808	0.1295	0.0542	0.0550
GOF	1.027	1.065	1.014	1.002	1.040
max. residual density peak and hole (e·Å^{-3})	0.612 and −0.395	1.117 and −1.477	2.731 and −3.276	0.865 and −0.802	1.049 and −0.616

compounds	**10**	**13**	**14**	**6c·C$_5$H$_{12}$**	**9c**	**11c**
formula	$C_{60}H_{51}BiO_3$	$C_{60}H_{66}Bi_2O_{12}$	$C_{30}H_{33}BiO_6$	$C_{77}H_{102}Bi_4Br_6O_8$	$C_{216}H_{160}Bi_{32}O_{56}$	$C_{90}H_{90}Bi_4Li_2O_{12}$
fw	1028.99	1393.06	698.54	2470.96	10338.80	2213.42
crystal syst	triclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	P-1	$P2_1/c$	$P2_1/c$	P-1	P-1	P-1
T, K	213(2)	223(2)	213(2)	218(2)	100(2)	100(2)
a, Å	11.2561(7)	12.5971(7)	8.1427(10)	12.77718(6)	19.155(2)	12.6805(9)
b, Å	13.3945(8)	17.4214(10)	24.223(3)	13.2642(6)	19.323(2)	13.1859(9)
c, Å	16.3952(10)	12.9355(8)	13.9470(18)	14.9861(6)	22.046(2)	14.0822(10)
α, deg	80.3940(10)	90.00	90.00	115.1620(10)	92.198(2)	109.9310(10)
β, deg	83.9810(10)	104.8130(10)	99.825(2)	97.3210(10)	114.670(2)	104.1920(10)
γ, deg	69.2090(10)	90.00	90.00	92.2500(10)	107.594(2)	101.7880(10)
V, Å^3	2275.7(2)	2744.5(3)	2710.5(6)	2266.74(17)	6939.6(13)	2036.2(2)
Z	2	2	4	1	1	1
d_{calcd}, mg·m^{-3}	1.502	1.686	1.712	1.810	2.474	1.805
μ, mm^{-1}	3.921	6.465	6.546	10.429	20.260	8.677
θ range (deg)	1.64–28.16	2.00–28.31	1.68–28.23	1.52–28.30	1.36–27.52	1.73–28.28
N measd	16674	27206	19515	14249	59825	20850
N ind	10309 [R(int) = 0.0292]	6548 [R(int) = 0.0322]	6361 [R(int) = 0.0334]	9372 [R(int) = 0.0244]	30862 [R(int) = 0.0451]	9083 [R(int) = 0.0232]
R_1	0.0392	0.0361	0.0326	0.0283	0.0444	0.0208
ωR_2	0.0862	0.0967	0.0729	0.0700	0.1202	0.0472
GOF	1.014	1.091	1.068	1.002	1.028	1.042
max. residual density peak and hole (e·Å^{-3})	2.222 and −1.173	1.411 and −1.142	1.205 and −0.955	1.755 and −1.277	3.734 and −2.649	1.206 and −0.956

General X-ray Crystal Structure Information. Data were collected on a Bruker SMART APEX CCD diffractometer or a Bruker SMART 1000 CCD diffractomer at variable low temperature using Mo Kα radiation. The crystallographic data and some details of the data collections and refinements of the structures are given in Table 4. Absorption corrections in all cases were applied by SADABS. Structures were solved using direct methods or the Patterson function, completed by subsequent difference Fourier syntheses, and refined by full matrix least-squares procedures on F^2. The highly disordered solvent pentane molecule located on an inversion center in **6c** was rendered using a diffuse contribution obtained by the program SQUEEZE.[72] The correction of the X-ray data by SQUEEZE, 65 electron/cell, is close to the required value, 42 electron/cell. In all structures, non-H atoms were refined with anisotropic thermal parameters. One of the —CH=CH$_2$ groups in **13** and two —CH$_2$— groups in **14** are disordered over two positions and were refined with the same occupations for both positions. H atoms were treated in calculated positions. All calculations were performed using the Bruker SHELXTL package.[73]

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

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