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Bismuth Allyloxides

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Bismuth allyloxides, $[Bi(OR)_3]$ with R = $CH_2CH{=}CH_2$, $CH(CH_3)CH{=}CH_2$, $C(CH_3)_2CH{=}CH_2$, and $CH_2CH{=}C(CH_3)_2$, can be prepared by alcoholysis of $[Bi(O^tBu)_3]$ and, in some cases, also via salt metathesis reactions starting from $BiCl_3$ and sodium allylates. They are readily soluble in common organic solvents, and NMR spectroscopic investigations do not provide any hint to aggregated species or any equilibria in solution. The majority of the compounds also proved volatile enough to be purified by sublimation. Crystal structure analyses, however, provided evidence for a high degree of aggregation in the solid state, which leads to large rings and chains as structural motifs.

Introduction

In the past decade bismuth alkoxide and siloxide compounds have received a lot of attention.[1-6] They were used (i) as starting materials for the synthesis of giant bismuth oxo clusters, which in turn represent models for small bismuth oxo particles,[5-7] (ii) for the synthesis of heterobimetallic compounds as small models for aggregated transition metal bismuthates,[8,9] and (iii) as precursors for bismuth oxide based materials.[8] One important class of mixed metal oxides containing bismuth are bismuth molybdates, which are employed as heterogeneous catalysts for the oxidation of propene to acrolein.[10-12] Allyloxy species are proposed as intermediates during the catalytic turnover,[11-13] and hence we became interested in the combination of allyloxy ligands and bismuth.

Experimental Section

General Procedure. All manipulations were carried out in a glovebox, or else by means of Schlenk-type techniques involving the use of a dry and oxygen-free argon atmosphere. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AV 400 NMR spectrometer (^1H, 400.1 MHz; $^{13}C\{^1H\}$, 100.6 MHz) in dry deoxygenated benzene-d_6 as solvent. The spectra were calibrated against the internal residual proton and natural abundance ^{13}C resonances of the deuterated solvent (benzene-d_6 δ_H 7.15 ppm, δ_C 128.0 ppm). Microanalyses were performed on a HEKAtech Euro EA 3000 elemental analyzer. Infrared (IR) spectra were recorded in the region 4000−400 cm^{-1} using solid samples prepared as KBr pellets with a Shimadzu FTIR-8400s spectrometer. The melting points were determined on a Stuart SMP10. Mass spectra were recorded on a quadrupole mass spectrometer Hewlett-Packard 5995 A for ions with m/z = 10−800 amu by ionization through electron collision at 70 eV (EI-MS).

Materials. Solvents were purified employing an MBraun SPS solvent purification system. $[Bi(O^tBu)_3]$[14] was prepared according to the literature procedure. $BiCl_3$, 2-propene-1-ol and 3-butene-2-ol were purchased from Merck, 3-methyl-2-butene-1-ol was obtained from Fluka, and 2-methyl-3-butene-2-ol was purchased from ABCR. $BiCl_3$ was sublimed, and all alcohols were dried over molecular sieve before use.

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Syntheses. [Bi(OCH$_2$CH=CH$_2$)$_3$] (1). HOCH$_2$CH=CH$_2$ (0.38 mL, 0.3 g, 5.6 mmol) was added dropwise via injection to a stirred solution of [Bi(O^{t}Bu)$_3$] (0.8 g, 1.87 mmol) in 15 mL of tetrahydrofuran (thf) at ambient temperature. During addition an exothermic reaction could be observed. The colorless solution was stirred at ambient temperature overnight. After removal of all volatile components, the residue was extracted into hexane (2 × 20 mL). The solvent of the extract was removed in vacuo to yield 0.59 g (1.55 mmol, 83%) of colorless microcrystalline **1**. Pure **1** could be obtained by sublimation (ϑ = 110 °C, $p = 5 \times 10^{-4}$ mbar).

^{1}H NMR (C$_6$D$_6$): δ = 6.24 (m, 3H, CH), 5.44 (dd, 3H, $^3J_{HH}{}^{trans}$ = 17.1 Hz, $^1J_{HH}$ = 1.5 Hz, CH=C$\underline{H}_2$), 5.36 (s, 6H, CH$_2$), 5.17 (dd, 3H, $^3J_{HH}{}^{cis}$ = 10.2 Hz, $^1J_{HH}$ = 1.5 Hz, CH=C$\underline{H}_2$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 142.4 (CH), 114.6 (CH=$\underline{C}$H$_2$), 65.3 (CH$_2$). IR (KBr): ν [cm^{-1}] = 3077, 3004, 2976, 2887, 2842, 2819, 2693, 1639, 1448, 1417, 1398, 1365, 1345, 1282, 1261, 1107, 1016, 990, 912, 804, 659, 560, 495 (br). Anal. Calcd for C$_9$H$_{15}$BiO$_3$ (M = 380.19 g mol^{-1}): C 28.43, H 3.98%. Found: C 28.06, H 3.92. Mp.: > 128 °C (decomposition).

[Bi(OCH(CH$_3$)CH=CH$_2$)$_3$] (2). Route A. A solid mixture of [NaOCH(CH$_3$)CH=CH$_2$] (1.41 g, 15 mmol) and BiCl$_3$ (1.58 g, 5 mmol) was dissolved in 50 mL of thf at ambient temperature, whereupon an exothermic reaction proceeded accompanied by precipitation of NaCl. After stirring the suspension for 3 h at ambient temperature all volatile components were removed in vacuum. Sublimation (ϑ = 90 °C, $p = 5 \times 10^{-4}$ mbar) of the raw product yielded analytically pure **2** (1.13 g, 2.68 mmol, 54%) in the form of a white microcrystalline solid.

Route B. HOCH(CH$_3$)CH=CH$_2$ (0.49 mL, 0.4 g, 5.6 mmol) was added dropwise via injection to a stirred solution of [Bi(O^{t}Bu)$_3$] (0.8 g, 1.87 mmol) in 15 mL of thf at ambient temperature. During addition a weakly exothermic reaction proceeded. The colorless solution was stirred at ambient temperature overnight. After removal of all volatile components the residue was dried in vacuo to yield 0.67 g (1.59 mmol, 85%) of colorless microcrystalline **2**. Pure **2** could be obtained by sublimation (ϑ = 90 °C, $p = 5 \times 10^{-4}$ mbar).

^{1}H NMR (C$_6$D$_6$): δ = 6.15 (ddd, 3H, $^3J_{HH}$ = 17.2, 10.2, 6.2 Hz, C$\underline{H}$=CH$_2$), 5.57 (m, 3H, C$\underline{H}$(CH$_3$)), 5.31 (ddd, 3H, $^3J_{HH}{}^{trans}$ = 17.2 Hz, CH$_2$), 5.03 (ddd, 3H, $^3J_{HH}{}^{cis}$ = 10.2 Hz, $^1J_{HH}$ = 1.9 Hz, CH$_2$), 1.45 (d, 9H, $^3J_{HH}$ = 6.2 Hz, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 147.2 ($\underline{C}$H=CH$_2$), 113.1 (CH$_2$), 70.4 ($\underline{C}$H(CH$_3$)), 27.6 (CH$_3$). IR (KBr): ν [cm^{-1}] = 3085, 3003, 2961, 2920, 2859, 1972, 1898, 1837, 1643, 1443, 1416, 1398, 1363, 1338, 1322, 1261, 1142, 1100, 1089, 1051, 997, 988, 917, 823, 813, 692, 586, 540, 493, 463. Anal. Calcd for C$_{12}$H$_{21}$BiO$_3$ (M = 422.27 g mol^{-1}): C 34.13, H 5.01%. Found: C 33.64, H 4.95. Mp.: 75−77 °C. HRMS (EI): Found m/z = 407.10831 [C$_{12}$H$_{21}$BiO$_3$−CH$_3$]$^+$, calcd for C$_{11}$H$_{18}$BiO$_3$ 407.10598. MS (EI): m/z (%) = 407.1 (5) [M-CH$_3$]$^+$, 351.1 (15) [Bi(OR)$_2$]$^+$, 335.9 (10) [Bi(OR)(OCHCHCH$_2$)]$^+$, 279.0 (35) [Bi(OR)]$^+$, 265.0 (5) [Bi(OCHCHCH$_2$)]$^+$, 209.0 (100) [Bi]$^+$, 71.1 (15) [OR]$^+$ with R = CH(CH$_3$)CHCH$_2$.

[Bi{OC(CH$_3$)$_2$CH=CH$_2$}$_3$] (3). Route A. A solid mixture of [NaOC(CH$_3$)$_2$CH=CH$_2$] (1.30 g, 12 mmol) and BiCl$_3$ (1.26 g, 4 mmol) was dissolved in 50 mL of thf at ambient temperature whereupon an exothermic reaction could be observed accompanied by precipitation of NaCl. After stirring the suspension for 3 h at ambient temperature, the solution was filtered off and all volatiles were removed from the filtrate to yield a white solid (1.54 g). Sublimation (ϑ = 80 °C, $p = 5 \times 10^{-4}$ mbar) of the raw product yielded analytically pure **3** (1.16 g, 2.50 mmol, 63%) in the form of a white microcrystalline solid.

Route B. HOC(CH$_3$)$_2$CH=CH$_2$ (2.07 mL, 1.70 g, 19.8 mmol) was added dropwise via injection to a stirred solution of [Bi(O^{t}Bu)$_3$] (2.82 g, 6.60 mmol) in 50 mL of thf at ambient temperature. The colorless solution was stirred at ambient temperature overnight. After removal of all volatile components the residue was dried in vacuo to yield a colorless microcrystalline solid. Sublimation (ϑ = 80 °C, $p = 5 \times 10^{-4}$ mbar) of the raw product yielded analytically pure **3** (2.72 g, 5.86 mmol, 89%) in the form of a white microcrystalline solid.

^{1}H NMR (C$_6$D$_6$): δ = 6.20 (dd, 3H, $^3J_{HH}$ = 17.4, 10.6 Hz, C$\underline{H}$=CH$_2$), 5.25 (dd, 3H, $^3J_{HH}{}^{trans}$ = 17.4 Hz, $^1J_{HH}$ = 1.5 Hz, CH$_2$), 4.96 (dd, 3H, $^3J_{HH}{}^{cis}$ = 10.6 Hz, $^1J_{HH}$ = 1.5 Hz, CH$_2$), 1.47 (s, 18H, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 150.5 (CH), 110.9 (CH$_2$), 75.0 ($\underline{C}$(CH$_3$)$_2$), 33.2 (CH$_3$). IR (KBr): ν [cm^{-1}] = 3085, 2964, 2923, 2861, 1462, 1411, 1370, 1354, 1281, 1255, 1221, 1176, 1135, 1003, 950, 919, 889, 736, 692, 570. Anal. Calcd for C$_{15}$H$_{27}$BiO$_3$ (M = 464.35 g mol^{-1}): C 38.80, H 5.86%. Found: C 38.74, H 5.86. Mp.: 61−62 °C. HRMS (EI): Found m/z = 449.15299 [C$_{15}$H$_{27}$BiO$_3$−CH$_3$]$^+$, calcd for C$_{14}$H$_{24}$BiO$_3$ 449.15292. MS (EI): m/z (%) = 449.2 (28) [M-CH$_3$]$^+$, 379.1 (50) [Bi(OR)$_2$]$^+$, 85.1 (22) [OR]$^+$ with R = C(CH$_3$)$_2$CHCH$_2$.

[Bi{OCH$_2$CH=C(CH$_3$)$_2$}$_3$] (4). HOCH$_2$CH=C(CH$_3$)$_2$ (1.4 mL, 1.2 g, 14 mmol) was added dropwise via injection to a stirred solution of [Bi(O^{t}Bu)$_3$] (2.0 g, 4.7 mmol) in 20 mL of thf at ambient temperature. During addition a weak exothermic reaction proceeded. The colorless solution was stirred at ambient temperature overnight. After removal of all volatile components the residue was extracted into hexane (2 × 15 mL). The solvent of the extract was removed in vacuo to yield 1.75 g (3.77 mmol, 81%) of pure colorless **4**.

^{1}H NMR (C$_6$D$_6$): δ = 5.81 (m, 3H, $^3J_{HH}$ = 6.7 Hz, CH), 5.50 (d, 6H, $^3J_{HH}$ = 6.4 Hz, CH$_2$), 1.79 (br, s, 9H, CH$_3$), 1.78 (br, s, 9H, CH$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 132.9 (C), 129.9 (CH), 60.8 (CH$_2$), 20.0/18.3 (CH$_3$). IR (KBr): ν [cm^{-1}] = 2967, 2910, 2876, 2851, 2724, 2668, 1667, 1448, 1374, 1363, 1319, 1259, 1243, 1195, 1109, 1043, 1016, 847, 777, 510, 442. Anal. Calcd for C$_{15}$H$_{27}$BiO$_3$ (M = 464.35 g mol^{-1}): C 38.80, H 5.86%. Found: C 38.57, H 5.87. Mp.: > 80 °C (decomposition).

Crystal Structure Determinations. Suitable single crystals of **1** were obtained by cooling a concentrated toluene solution to −30 °C. Evaporation of the solvent from a saturated solution of **4** in toluene led to colorless crystals that were suitable for an X-ray diffraction analyses. The crystal data were collected on a Stoe IPDS 2T diffractometer using Mo$_{K\alpha}$ radiation, λ = 0.71073 Å. In both cases, the structures were solved by direct methods (SHELXS-97)[15] and refined versus F^2 (SHELXL-97)[16] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. The structure **1** is of somewhat lower quality in comparison to the one of its congener **4** because of disorder within the allylic residues as well as a higher number of Bi atoms in the unit cell (higher absorption). Relevant crystallographic data are collected in Table 1.

Results and Discussion

At the beginning of our studies bismuth(III) allyloxides were unknown, perhaps because of an expected (or observed, vide infra) high tendency toward aggregation that often leads to low solubilities. In general metal alkoxides often oligomerize or polymerize, if the organic residues employed do not prevent this through their bulkiness; in the latter case the Bi atoms remain three-coordinated with almost orthogonal Bi−O bonds.[2,5,6] If the residues are not sterically demanding, additional interactions with the Lewis-basic alkoxide ligands of a second (or even a third) molecule occur. Interactions of this type are called *secondary interactions*[17] and arise from the pronounced Lewis

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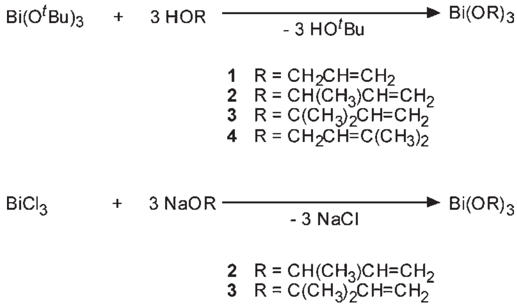
Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of **1** and **4**

	1	**4**
Formula	$C_{36}H_{60}Bi_4O_{12}$	$C_{15}H_{27}BiO_3$
weight, g mol^{-1}	1520.76	464.35
temp, K	100(2)	100(2)
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	12.4572(9)	10.4820(9)
b, Å	12.5744(8)	7.0055(3)
c, Å	16.9058(14)	24.1062(15)
α, deg	99.202(6)	90
β, deg	98.238(6)	98.315(6)
γ, deg	117.021(5)	90
V, Å^3	2257.4(3)	1751.5(2)
Z	2	4
density, g cm^{-3}	2.237	1.761
$\mu(\mathrm{Mo}_{K\alpha})$, mm^{-1}	15.597	10.068
$F(000)$	1408	896
GoF	0.947	1.017
R_1 [$I > 2\sigma(I)$]	0.0612	0.0245
wR_2 [all data]	0.1555	0.0577
$\Delta\rho_{\mathrm{min}}/\Delta\rho_{\mathrm{max}}$, e Å^{-3}	2.531/−4.056	1.980/−2.155

acidity of the bismuth center. From structural and electronic considerations, the relevant acceptor orbitals at the bismuth center are thought to be Bi−O σ*-orbitals.[18] Hence, for an ideal overlap an O···Bi−O angle of 180° would be required; a deviation of the angles from linearity reflects a decreased strength of the interactions. In principle the three Bi−O primary bonds in bismuth(III) alkoxides allow for three further secondary bonds.[19] If only two such bonds are formed the resulting 3 + 2 coordination environments are mostly described as square pyramidal or as trigonal bipyramidal.[6,19−22] Correspondingly, the coordination spheres at bismuth atoms with six-coordinated ligands (3 + 3 coordination) should ideally be octahedral, but, as the structural motifs of the aggregated assembles or the organic residues involved often do not allow for such an arrangement, many severely distorted structures were reported, too (vide infra).[14,23] As a result of secondary bonding bismuth alkoxides often form cyclic structures[3,4,20,24] or one-dimensional chains[14,21] containing $Bi_2(\mu\text{-OR})_2$ units. Interactions of the bismuth centers with π-donor functions[2,20,25] as part of the alkoxidic residues can further support aggregation, if they occur. The finding, that initial attempts to prepare $[Bi(OCH_2CH{=}CH_2)_3]$, **1**, via reaction of $BiCl_3$ with the corresponding sodium alcoholate only led to insoluble solids, which could not be characterized adequately, was therefore not contrary to the expectations. However, it might have been only a result of the presence of NaCl formed in the course of the salt metathesis and being incorporated into aggregated structures or of the formation of insoluble "ate-complexes": In the course of further investigations, the synthesis of the homoleptic bismuth(III) alkoxide **1** was achieved by alkoxide exchange reactions between $[Bi(O^tBu)_3]$ and the corresponding allyl alcohol $HOCH_2CH{=}CH_2$ (ratio 1:3) in thf in near quantitative yields (Scheme 1). $[Bi(OCH_2CH{=}CH_2)_3]$, **1**, proved to be sufficiently volatile to allow for a purification by sublimation, and unlike classical bismuth(III) alkoxides $[Bi(OR)_3]$ (R = Me, Et, ^{i}Pr, ^{t}Bu),[14,26] which display low solubilities in nonpolar solvents (partly in polar media, too), **1** is readily soluble in all common organic solvents, which might be indicative of a monomeric character in solution. Consistently, NMR spectra showed only one set of signals characteristic for an allyl group.

Scheme 1



To obtain structural information concerning **1** in the solid state an X-ray diffraction analysis was carried out with single crystals obtained by cooling of a concentrated toluene solution to −30 °C. A novel chain structure, assembled from cycles composed of 10 bismuth atoms was found. A section of this structure is shown in Figure 1, focusing on the repeating ten-membered-cycle. Relevant bond lengths, distances, and angles are listed in the caption of this figure.

The bismuth atoms within the cycles exhibit two different coordination environments. The coordination geometries at the bismuth atoms Bi1 and Bi3 are best described as 3 + 3 coordination, whereas Bi2 and Bi4 show 3 + 2 coordination. Exemplary, Bi2 and Bi3 are chosen for a more detailed discussion of these coordination environments (Figure 2).

As mentioned before, in the literature, coordination spheres of bismuth centers ligated by five O-donor ligands are generally referred to as square pyramidal or trigonal bipyramidal.[14,22,27] In α-Bi_2O_3 there are two symmetrically distinct bismuth atoms. One of these has a coordination number of five, and the corresponding bismuth centers have square pyramidal ligations (distorted octahedra with one of the corners removed),[28] and the same is found for Bi2 with bond angles of 67.06(18), 83.4(2), 86.6(2), and 120.3(2)° in the basal plane and angles between the apical oxygen atom, the bismuth atom, and the basal oxygen atoms of 69.4(2), 87.5(2), 89.7(2), and 90.7(2)°. Short primary bonds are formed to O4, O5, and O6 (2.084(6), 2.104(5), and 2.156(5) Å) and opposite to the ligand atoms O5 and O6, longer secondary bonds are formed to O1 (2.573(5) Å) and O7 (2.656(5) Å, Figure 2).

The bismuth atom Bi3 is coordinated by six $OCH_2CH{=}CH_2$ ligands. Bismuth atoms with six nearest neighbor oxo atoms were discussed differently in the literature. For example Mehring and co-workers described the coordination geometry

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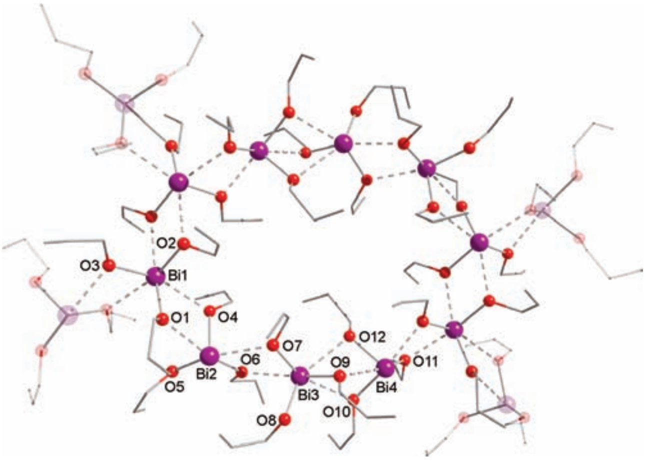

Figure 1. Molecular structure of **1**. All hydrogen atoms were omitted for clarity. The labeled atoms represent the asymmetric unit within the chain structure. Selected bond lengths and atom distances /Å and angles /deg: Bi1−O1 2.199(6), Bi1−O2 2.167(6), Bi1−O3 2.152(5), Bi2−O4 2.084(6), Bi2−O5 2.104(5), Bi2−O6 2.156(5), Bi3−O7 2.155(5), Bi3−O8 2.067(7), Bi3−O9 2.162(5), Bi4−O10 2.146(6), Bi4−O11 2.169(6), Bi4−O12 2.064(4), Bi1−O4 2.708(5), Bi2−O1 2.573(5), Bi2−O7 2.656(5), Bi3−O6 2.576(4), Bi3−O10 2.723(5), Bi3−O12 2.755(5), Bi4−O9 2.473(5), Bi1−Bi2 3.9637(6), Bi2−Bi3 3.9068(5), Bi3−Bi4 3.6073(5), O1−Bi1−O2 90.9(3), O2−Bi1−O3 88.9(2), O1−Bi1−O3 86.7(2), O4−Bi2−O5 90.7(2), O5−Bi2−O6 86.6(2), O4−Bi2−O6 89.7(2), O7−Bi3−O8 93.2(2), O8−Bi3−O9 85.4(2), O7−Bi3−O9 86.88(18), O10−Bi4−O11 88.9(2), O11−Bi4−O12 92.0(2), O10−Bi4−O12 82.79(19), Bi1−O1−Bi2 112.1(3), Bi1−O4−Bi2 110.9(2), Bi2−O6−Bi3 111.0(2), Bi2−O7−Bi3 108.1(2), Bi3−O9−Bi4 102.0(2), Bi3−O10−Bi4 94.88(19), Bi3−O12−Bi4 95.89(18).

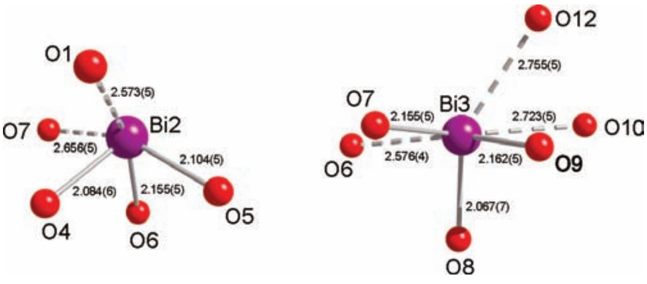

Figure 2. Bismuth−oxygen polyhedra observed for Bi2 and Bi3 within **1** including bond distances given in Å. The polyhedron associated with Bi1 is similar to that of Bi3 and the one of Bi4 is similar to that of Bi2.

at the six-coordinated bismuth atom in [Bi($OSiMe_3$)$_3$] as a trigonal pyramid with three oxygen atoms (Bi−O bond lengths of 2.041(3)−2.100(3) Å) and a stereochemically active lone pair of electrons occupying the corners. Three additional oxygen atoms (Bi···O secondary bonds with lengths of 2.908(3)−3.230(3) Å) associated with neighboring molecules complete the coordination environment, but do not influence the coordination polyhedron at the bismuth atom in its first coordination shell, significantly.[4] Hanna and co-workers described the coordination of four bismuth atoms found to be surrounded by six O-ligands within an areneoxide ligated $Bi_{32}O_{56}$ cluster as distorted pentagonal pyramidal with Bi−O bonds in the range of 2.116(8)−2.667(10) Å and with arene residues shielding the empty coordination sites.[6] Furthermore Whitmire et al. defined the coordination spheres of the bismuth atoms in $NaBi_4(\mu_3\text{-}OR)_2(OR)_9(THF)_2$ composed of six oxygen atoms and one lone pair of electrons as distorted pentagonal bipyramidal.[22] Beside the five-coordinated Bi atoms occurring in α-Bi_2O_3 as discussed above, there is a second type of Bi atoms, which are bound to six oxygen ligands and possess heavily distorted octahedral coordination environments.[28] A comparable structural motif was found for the monomeric [Bi(OC(CH_3)$_2$$CH_2OCH_3$)$_3$], where six oxygen atoms of the three chelating ligands form a heavily distorted octahedron around the central bismuth atom.[23]

As the Bi2 center in **1**, also Bi3 exhibits three short, primary contacts, namely, to O7, O8, and O9 with bond lengths of 2.155(5), 2.067(7), and 2.162(5) Å and angles close to 90° (85.4(2), 86.88(18), and 93.2(2)°), and insofar the situation also resembles the one found for the trimethylsilanolate bismuth derivative synthesized by Mehring et al.[4] Similarly to the latter for Bi3 in **1** secondary bonds are observed, too, which, however, have much shorter lengths. O6 is in an almost ideal position for such bonding forming an angle of 152.43(19) ° with O9 and an angle of 68.65(17) ° with O7, that is, it is located *trans* to O9. O10 and O12, however, are shifted significantly from the orthogonal axes of an octahedron. Hence, secondary bonding is less efficient, and the distances to Bi3 are longer (2.723(5) and 2.755(5) Å, Figure 2). This kind of arrangement probably has its origin in the restrictions occurring for Bi3 as part of the ring system and not in a stereoactive lone pair of electrons.

Generally in alkoxide chemistry metal-oxo bonds belonging to terminal alkoxide ligands are shorter than those of bridging ones, and consistently the Bi2−O5 and Bi3−O8 distances (2.104(5) and 2.067(7) Å) are the shortest ones in **1** (compare Figures 1 and 2).[14,20,29] The observed secondary bismuth−oxygen bonds lie within the range 2.473(5)−2.755(5) Å.

With respect to the cyclic arrangement of the [Bi(OCH_2CH=CH_2)$_3$] units within the structure of **1** it may be noted that on aggregation of bismuth alkoxides in the solid state most frequently dimers containing $Bi_2(\mu\text{-}OR)_2$ cores are generated like in [Bi(O$CH_2$$CH_2OCH_3$)$_3$],[14,21] [{Bi(OCH($CF_3$)$_2$)$_3$(thf)}$_2$], and [{Bi($OC_6F_5$)$_3$($C_7H_8$)}$_2$].[20,24] [Bi(OSiMe$_3$)$_3$] forms a trimer in the course of weak intermolecular Bi···O interactions (vide supra) and is thus an example for a loosely associated trinuclear cycle.[4] So far the largest cycles composed of bismuth alkoxide units had been observed within the crystal structure of the ethanol solvate of [Bi(OEt)$_3$], [Bi(OEt)$_3$]$_8$·(7+*x*) EtOH, displaying eigth-membered bismuth rings.[3] Hence, the cyclic decamers found as the essential units of the structure adoped by **1** exhibit a so far unreached ring-size for bismuth alkoxides.

The chains generated by the connection of the Bi_{10} rings and their arrangement in the solid phase is shown in Figure 3.

Having isolated and characterized the parent allyloxy compound **1**, we were interested in the effects of introducing methyl groups at the allylic residues, since such subtle changes within the organic residues of metal alkoxides were often observed to have pronounced effects structurally and electronically.[1] Treatment of [Bi(O^{t}Bu)$_3$] with 3 equiv of 3-butene-2-ol led to [Bi(OCH(CH_3)CH=CH_2)$_3$], **2**, which can be formally derived from **1** by a H/CH_3 exchange in the allylic position, in 85% yield. Unlike **1**, **2** could also be obtained via a metathesis reaction between $BiCl_3$ and the corresponding sodium salt in 54% yield (Scheme 1). **2** exhibits good

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(29) Evans, W. J.; Hain, J. H., Jr.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1628.

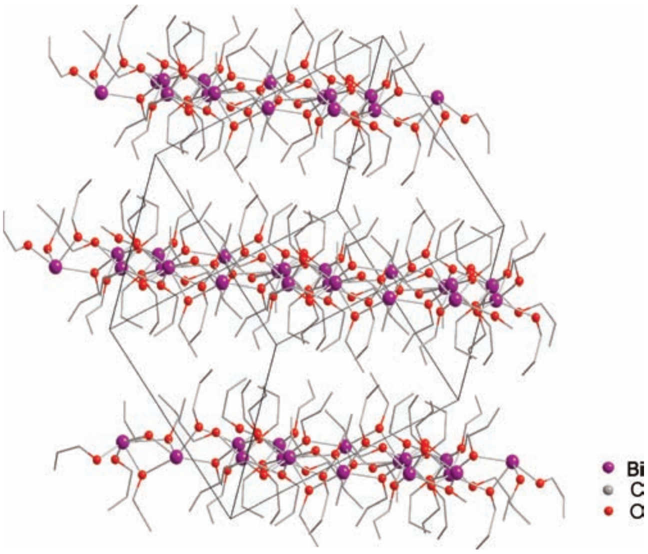

Figure 3. Structure of **1** within the unit cell showing the isolated chains and their parallel arrangement.

solubility, too, and it could also be further purified by sublimation in vacuum. As in case of **1** only one set of signals, very similar to the one displayed by [NaOCH(CH$_3$)-CH=CH$_2$], was observed for the allylic residue in the NMR spectra of **2**. To test, whether this is due to a highly dynamic ligand exchange within a more complex structure or to rapid equilibrium between several species, variable temperature NMR studies were performed for toluene-d_8 solutions of **2**. However, the only observations that could be made on lowering of the temperature were a shift of all signals to lower field. At the same, as a result of decreased solubility, they become increasingly broader, and at −40 °C a shoulder grows in for the signal of the allylic proton, which separates itself at −50 °C (see Supporting Information).

Colorless crystals of **2** that were suitable for an X-ray diffraction analysis could be obtained by slow evaporation of the solvent from a saturated solution of **2** in toluene. However, despite repeated measurements with various crystals (hexagonal crystal system $a = b = 21.122(3)$ Å, $c = 7.3630(10)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 2844.3(7)$ Å^3, $Z = 4$) the data obtained never allowed for a complete structure refinement and a reliable solution because of serious crystal structure disorder. Transformation of the pseudohexagonal crystal system into a monoclinic one at least enabled identification of the bismuth positions, which could be refined anisotropically, and a few oxygen atom positions belonging to the allyl alcohol residues could be determined, too. According to the obtained structural information [Bi(OCH(CH$_3$)CH=CH$_2$)$_3$], **2**, is polymeric in the solid state, as it builds up chain-like aggregates with at least two μ_2-bridging alkoxo ligands, which were also observed for the bismuth(III) alkoxide [Bi{OCH$_2$CH=C(CH$_3$)$_2$}$_3$], **4** (vide infra).

When allyl alcohol doubly methylated in the allylic position (i.e., 2-methyl-3-butene-2-ol) was employed for the alcoholysis of [Bi(O^{t}Bu)$_3$] the homoleptic bismuth(III) alkoxide [Bi{OC(CH$_3$)$_2$CH=CH$_2$}$_3$], **3**, was obtained. **3** could alternatively be accessed by salt metathesis reaction between BiCl$_3$ and 3 equiv of the corresponding sodium salt in 63% yield (Scheme 1). Again in the NMR spectra of toluene-d_8 solutions no indications for asymmetric structures or more than one species could be found. However, on cooling to 0 °C a signal of lower intensity separated from the singlet produced by the methyl groups, and at −50 °C shoulders developed also for the vinyl resonances, which partly turned into resolved signals on further cooling (see Supporting Information). Hence, either an equilibrium or an asymmetric structure is frozen out at that temperature. **3** was sufficiently volatile to allow for purification by sublimation, and single crystals were obtained by evaporation of the solvent from a saturated solution of **3** in thf or toluene. These were extremely sensitive to hydrolysis, though, and decomposed already during crystal preparation on the light-optical microscope even at low temperatures.

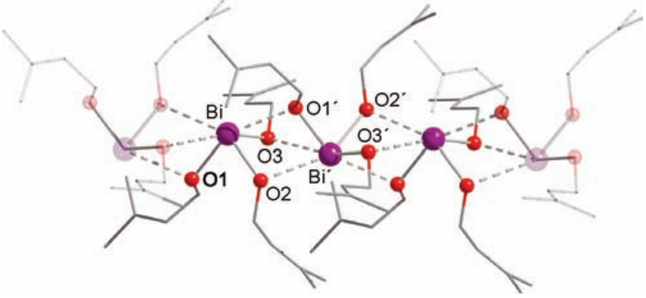

Figure 4. Molecular structure of **4**. All hydrogen atoms were omitted for clarity. Selected bond lengths and distances /Å and angles /deg: Bi−O1 2.159(2), Bi−O2 2.131(2), Bi−O3 2.162(2), Bi−O1′ 2.570(2), Bi−O2′ 2.746(2), Bi−O3′ 2.657(2), Bi−Bi′ 3.5637(2), O1−Bi−O2 87.28(9), O2−Bi−O3 86.66(9), O1−Bi−O3 88.89(9), Bi−O1′−Bi′ 97.42(9), Bi−O2−Bi′ 93.03(8), Bi−O3−Bi′ 94.82(9), O1−Bi−O1′ 150.22(7).

In the next step the two vinylic protons were (formally) exchanged by methyl groups, that is, [Bi(O^{t}Bu)$_3$] was treated with 3 equiv of 3-methyl-2-butene-1-ol. This quantitatively led to [Bi{OCH$_2$CH=C(CH$_3$)$_2$}$_3$], **4**, which was isolated in the form of a white microcrystalline solid in 81% yield. In contrast to **1**−**3** further purification of **4** through sublimation was not possible: **4** decomposes in vacuum at temperatures above 80 °C needed for evaporation. However, **4** could be obtained in analytically pure form by extraction of the crude product with hexane, wherein the starting material [Bi(O^{t}Bu)$_3$] is only poorly soluble. Only one signal set for a CH$_2$CH=C(CH$_3$)$_2$ unit was observed in the NMR spectra.

Evaporation of the solvent from a saturated toluene solution of **4** led to colorless crystals that were suitable for an X-ray diffraction analysis. A chain structure was found as in the case of **2**, whose structure, however, had eluded complete solution (vide supra), while the structure of **4** could be determined with sufficient quality. A section of one of the infinite [Bi(OCH$_2$CH=C(CH$_3$)$_2$)$_3$]$_\infty$ chains, where [Bi{OCH$_2$CH=C(CH$_3$)$_2$}$_3$] represents the repeating unit, is shown in Figure 4.

At first approximation all bismuth atoms show a 3 + 3 coordination by six oxygen atoms (Figure 5). As in the case of Bi3 in **1**, three of these oxygen atoms (O1, O2, and O3) form short bonds to the bismuth center (2.159(2), 2.131(2), and 2.162(2) Å) and the O−Bi−O angles involved are close to 90° (87.28(9), 86.66(9), and 88.89(9)°). Hence, they can be considered as primary bonds constructed from bismuth p-orbitals. Furthermore, there are secondary contacts to O1′, O2′, and O3′ with unfavorable angles, and correspondingly the distances are much longer (2.570(2), 2.657(2), and 2.746(2) Å). The coordination environment can thus be described as a heavily distorted octahedron as discussed for

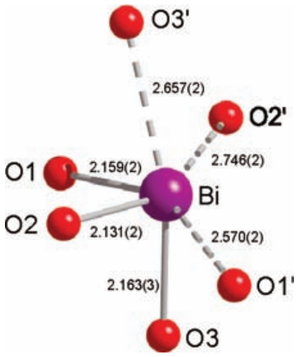

Figure 5. Coordination environment around the bismuth center formed by oxygen atoms in **4** including bond distances given in Å. Observed angles/deg: O1−Bi−O2′ 66.86(8), O2−Bi−O1′ 70.81(8), O1′−Bi−O2′ 137.21(7), O3−Bi−O3′ 157.35(6).

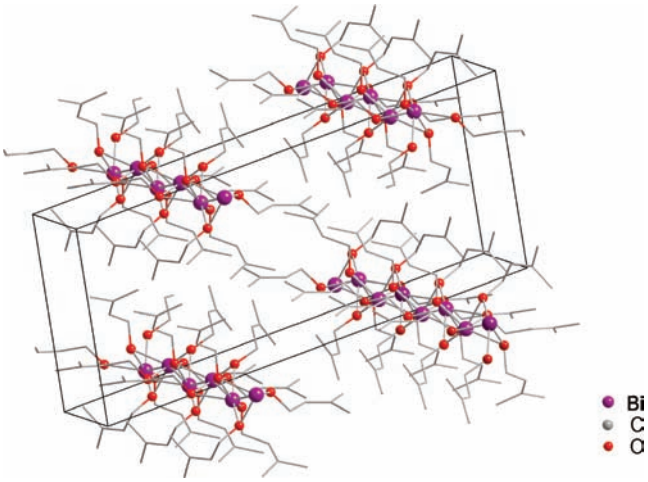

Figure 6. View showing the isolated skew chains of **4** along the *b* axes.

the six-coordinated bismuth atoms in α-Bi_2O_3[28] and $[Bi(OC(CH_3)_2CH_2OCH_3)_3]$.[23]

The repeating $[Bi\{OCH_2CH{=}C(CH_3)_2\}_3]$ units are connected to each other through three asymmetric μ_2-alkoxy bridges, that is, there are no terminal bimuth alkoxo ligands within the structure of **4**. Figure 6 illustrates the resulting "zigzag" chains extended along the *b* axis of the unit cell and the packing therein. Hence, a similar arrangement of the $[Bi(OR)_3]$ units can now be assumed for compound **2**.

Conclusions

A so far unknown class of bismuth alkoxides, the bismuth allyloxides, has been made accessible and investigated. Four representatives could be prepared via salt metathesis and/or alcoholysis reactions. While their high-solubilities, even in nonpolar solvents, and their NMR spectra recorded point to monomeric, or at least to low-molecular, symmetric units in solution, they are highly aggregated in the solid state forming large rings connected to chains (**1**) or skewed zigzag chains (**2**, **4**). However, apparently the assembly is only loose considering the remarkable volatility of **1**−**3**. In none of the structures were Bi···C=C π interactions observed. In future studies these bismuth compounds can now be used as synthons, for instance, for the preparation of compounds modeling species suggested to occur on the surfaces of catalysts employed for the propene oxidation or for the synthesis of functionalized bismuth alkoxides. On the other hand the allylic residues can also be utilized for the complexation of other metals and thus for the preparation of heterometallic precursor compounds.

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Supporting Information Available: X-ray crystallographic information files containing full details of the structural analysis of the complexes **1** and **4**. Furthermore experimental details for the syntheses and analytical data of the used sodium salts $[NaOCH(CH_3)CH{=}CH_2]$ and $[NaOC(CH_3)_2CH{=}CH_2]$, the best structure obtained by the structure refinement of **2**, and variable temperature NMR spectra of **2** and **3** are provided. This material is available free of charge via the Internet at http://pubs.acs.org.