

# Sterically crowded aryloxides of aluminum: intramolecular coordination of bidentate ligands

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Dedicated to Professor Pasykiewicz for his contributions to the chemistry of aluminum

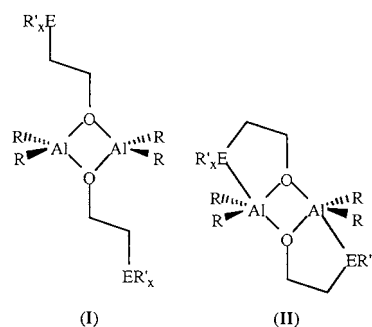
## Abstract

Reactions of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  ( $\text{BHT-H} = \text{HOC}_6\text{H}_2\text{-2,6-}^i\text{Bu}_2\text{-4-Me}$ ) with  $\text{HOCH}_2\text{CH}_2\text{EMe}_x$  ( $\text{E} = \text{O}, \text{S}, x = 1$ ;  $\text{E} = \text{N}, x = 2$ ) yield dimeric species,  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**2**),  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$  (**3**),  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{SMe})]_2$  (**4**), respectively or  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**5**),  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$  (**6**) and  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{SMe})(\mu\text{-OCH}_2\text{CH}_2\text{SMe})]_2$  (**7**), respectively, depending on the stoichiometry of the reaction. The non-bridged donor atoms interact intramolecularly to form five-coordinate aluminum centers. A mixture of  $(\text{BHT})\text{Li}(\text{Et}_2\text{O})$  and  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ , formed from the reaction of  $\text{LiAlH}_4$  and  $\text{BHT-H}$ , reacts with the aforementioned alcohols to yield the monomeric structures  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Li}$  (**8**),  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2\text{Li}$  (**9**),  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}$  (**10**), respectively. If the reaction is carried out with an excess of  $\text{HOCH}_2\text{CH}_2\text{SMe}$ , the solvate of compound **10** is formed,  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}(\text{HOCH}_2\text{CH}_2\text{SMe})$  (**11**). The lithium cation in compounds **8–11** is stabilized in the structure by formation of bonds with both the anionic oxygens as well as the neutral donor ligands. The bond valencies have been calculated for Al and Li in compounds **8** and **11**. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Aluminum; Aryloxide; Sterically crowded

## 1. Introduction

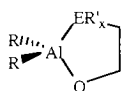
It has been widely reported that the reaction of non-delocalized ligand precursors containing both anionic and neutral Lewis base termini with aluminum alkyls produces compounds in which both termini are coordinated to aluminum [1–6]. We have recently studied a subset of these compounds: those containing substituted alkoxide ligands such as  $[\text{OCH}_2\text{CH}_2\text{ER}'_x]^-$ , where E is oxygen, sulfur or nitrogen [7–10]. These compounds have either four- or five-coordinate aluminum centers (**I** and **II**, respectively) depending on the steric bulk of the substituent on the aluminum and the heteroatom, as well as the identity of the heteroatom itself.



Although these compounds were useful in understanding the effects of steric bulk and the identity of the heteroatom on the strength of the intramolecular interaction that forms [7], they are not models for latent Lewis acidity. Latent Lewis acidity is a term used to describe the ability of an electron-precise molecule to undergo heterolytic bond cleavage to generate an electron-deficient, Lewis acidic site [11]. The dimeric struc-

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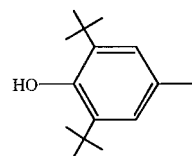
tures are not latent Lewis acids because the cleavage of the intramolecular bond results in a four-coordinate aluminum center that is itself not Lewis acidic, as indicated by the lack of reactivity of these compounds with external Lewis bases. In the case of the cage alumoxanes, latent Lewis acidity explains their co-catalytic ability and is a direct consequence of the ring strain present in the cluster [11]. In order to synthesize latent Lewis acids, cyclic, monomeric compounds with intra-molecular coordination sites must be made (e.g. **III**). The energy barrier necessary to cleave the dimeric structure and produce a monomer has been calculated for  $[\text{H}_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OH})_2]$  [12] to be in the order of  $254 \text{ kJ mol}^{-1}$ . To overcome this large barrier, a sufficiently bulky group must be present on the aluminum.



(III)

Previous work in the Barron group has focused on the sterically demanding aryloxy, 2,6-di-*tert*-butyl-4-methylphenol (**IV**, BHT-H from the trivial name

butylated hydroxytoluene), to stabilize otherwise inaccessible monomeric compounds by inhibition of oligomerization [13,14].



(IV)

For the following studies, BHT was chosen as the substituent on the aluminum not only for its steric bulk but also because the coordination sphere of aluminum would then closely mimic that in cage alumoxanes. Herein, we outline our attempt to synthesize potentially latent Lewis acidic aluminum compounds with ligands containing both anionic and neutral Lewis base termini using BHT as the substituents on the aluminum.

## 2. Results and discussion

The reaction of an excess of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  (prepared via the reaction of BHT-H and  $\text{NaAlH}_4$ , see Section 4) with  $\text{HOCH}_2\text{CH}_2\text{EMe}_x$  ( $\text{E} = \text{O}, \text{S}, x = 1$ ;  $\text{E} = \text{N}, x = 2$ ) yields a mixture of products which may be characterized by  $^1\text{H-NMR}$  spectroscopy. In addition to the products containing the functionalized alkoxide (see below), unreacted starting material,  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  [15], and BHT-H are seen in all samples irrespective of the starting alcohol, while a third, previously uncharacterized, product is also formed where  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  is employed in excess. This third product (compound **1**) may be separated from the reaction mixture by selective recrystallization from dichloromethane. Its  $^1\text{H-NMR}$  spectrum shows that the ratio of BHT groups to aluminum hydride is 2:1 and the mass spectrum shows peaks due to  $2\text{M}^+ - 2\text{Me}$  ( $m/z = 684$ ) and  $\text{M}^+ - \text{Me}$  ( $m/z = 451$ ), consistent with the dimer, i.e.  $[(\text{BHT})_2\text{Al}(\text{H})]_2$  (**1**). If a dimer is maintained in the solution then the presence of a single set of resonances for the BHT ligand suggests that the hydrides are bridging. However, while the IR spectroscopy confirms the presence of an aluminum hydride functionality, its frequency ( $\nu_{\text{Al-H}} = 1844 \text{ cm}^{-1}$ ) is characteristic of a terminal hydride ( $\nu_{\text{Al-H}} = 1920\text{--}1800 \text{ cm}^{-1}$ ) [16]. Unfortunately, we were unable to obtain crystals suitable for X-ray diffraction studies.

Based upon spectroscopic and X-ray analysis, the products synthesized containing the functionalized alkoxide are  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$ , where  $\text{EMe}_x = \text{NMe}_2$  (**2**),  $\text{OMe}$  (**3**), and  $\text{SMe}$  (**4**). The aluminum hydride stretch is seen at  $1828 \text{ cm}^{-1}$  for compound **4**, which is consistent with a terminal hydride [16], and the dimeric nature of compound **2** is confirmed by the X-ray crystallography.

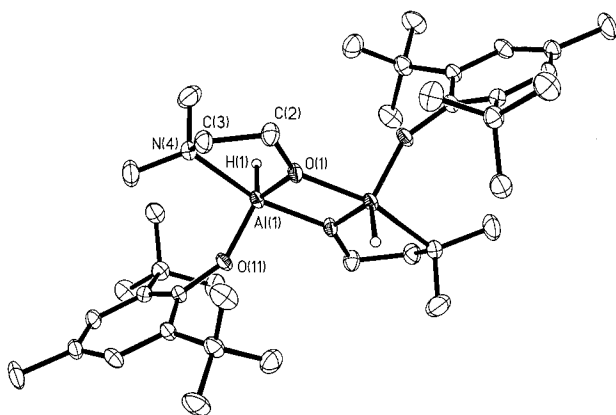


Fig. 1. Molecular structure of  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**2**). Thermal ellipsoids are given at the 30% level and hydrogen atoms are omitted for clarity.

Table 1

Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$  (**2**)

Bond lengths			
Al(1)–O(1)	1.832(3)	Al(1)–O(1')	1.913(3)
Al(1)–N(4)	2.196(4)	Al(1)–O(11)	1.744(3)
Al(1)–H(1)	1.61(2)		
Bond angles			
O(11)–Al(1)–O(1)	125.2(2)	O(11)–Al(1)–O(1')	95.8(1)
O(1)–Al(1)–O(1')	74.8(1)	O(11)–Al(1)–N(4)	99.5(1)
O(1)–Al(1)–N(4)	80.1(1)	O(1')–Al(1)–N(4)	154.9(1)
O(1)–Al(1)–H(1)	118(1)	O(1')–Al(1)–H(1)	99(1)
O(11)–Al(1)–H(1)	117(1)	N(4)–Al(1)–H(1)	92(1)
Al(1)–O(1)–Al(1')	105.1(1)		

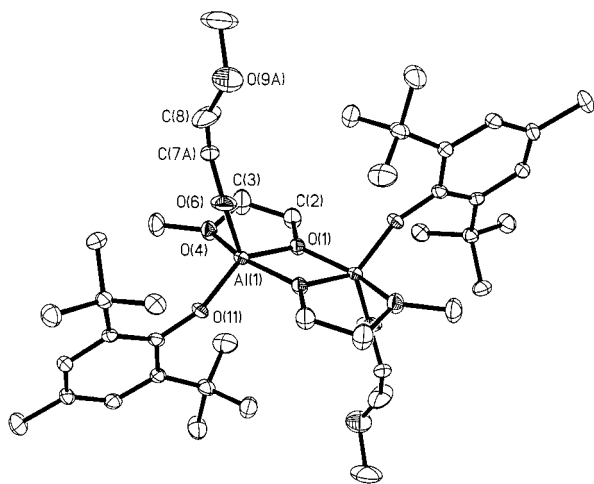
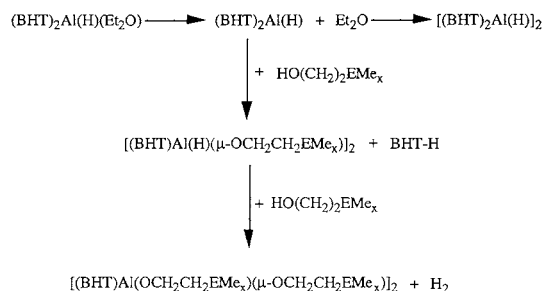


Fig. 2. Molecular structures of  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]$  (**6**). Thermal ellipsoids are given at the 30% level and hydrogen atoms are omitted for clarity.

The molecular structure of  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2]$  (**2**), is shown in Fig. 1; selected bond lengths and angles are given in Table 1. Compound **2** exists as a tri-cyclic centrosymmetric dimer with the neutral donor forming an intramolecular bond with the aluminum center. The geometry about each aluminum atom is a distorted trigonal bipyramidal with O(1') and N(4) occupying the axial positions [ $\text{O}(1')\text{-Al}(1)\text{-N}(4) = 154.9^\circ$ ] and H(1), O(1) and O(11) defining the equatorial sites. The sum of the bond angles between the equatorial ligands is  $360.2^\circ$ . The distortion about the aluminum center results from the planarity of the  $\text{Al}_2\text{O}_2$  core. The bond length of the intramolecular coordination is 2.196 Å and that of the terminal Al–H is 1.61 Å, which is comparable to the values obtained for similar dimeric terminal aluminum hydrides [16–20]. The Al–O distance, and those in the other structures discussed herein, are comparable to the values reported for other Al–BHT compounds [21–24].

Table 2  
Selected bond lengths (Å) and angles ( $^\circ$ ) for  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{OMe})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]$  (**6**)

Bond lengths			
Al(1)–O(1)	1.844(3)	Al(1)–O(1')	1.874(3)
Al(1)–O(11)	1.730(3)	Al(1)–O(4)	2.025(3)
Al(1)–O(6)	1.704(3)		
Bond angles			
O(1')–Al(1)–O(1)	75.0(1)	O(1')–Al(1)–O(4)	152.6(1)
O(1')–Al(1)–O(6)	103.4(2)	O(1')–Al(1)–O(11)	97.5(1)
O(4)–Al(1)–O(6)	92.8(2)	O(4)–Al(1)–O(11)	94.8(1)
O(4)–Al(1)–O(1)	78.4(1)	O(6)–Al(1)–O(11)	116.0(2)
O(6)–Al(1)–O(1)	112.8(2)	O(11)–Al(1)–O(1)	131.0(2)
Al(1)–O(1)–Al(1')	104.9(1)	Al(1)–O(1)–C(2)	133.2(3)
Al(1)–O(6)–C(7A)	146.4(5)	Al(1)–O(6)–C(7B)	151.5(5)
Al(1)–O(11)–C(11)	159.3(3)		



Scheme 1. Reaction scheme for  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  with  $\text{HO}(\text{CH}_2)_2\text{EMe}_x$ .

If the reaction of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  with  $\text{HOCH}_2\text{-CH}_2\text{EMe}_x$  is carried out in a stoichiometric manner in an exact 1:1 ratio, three products are seen by NMR spectroscopy. The minor products are BHT-H, and  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  (**2–4**), while the major products are the dimeric structures  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{EMe}_x)(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  [ $\text{EMe}_x = \text{NMe}_2$  (**5**), OMe (**6**) and SMe (**7**)]. Compounds **5–7** may be separated by selective recrystallization from dichloromethane or by washing with pentane, a solvent in which  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  is insoluble. The dimeric structure of the major product is verified by the X-ray crystallographic structure of compound **6**.

The molecular structure of  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{-CH}_2\text{OMe})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]$  (**6**) is shown in Fig. 2, and selected bond lengths and angles are given in Table 2. As with compound **2**, compound **6** is a tri-cyclic centrosymmetric dimer with the neutral donor atom forming an intramolecular bond with the aluminum atom. Also like compound **2**, the geometry at the aluminum atoms approximates trigonal bipyramidal with the chelating neutral oxygen O(4) and the bridging oxygen O(1') occupying the axial positions. The length of the intramolecular coordination, Al(1)–O(4) [2.025(3) Å] is indicative of a stronger interaction than that seen in  $[(t\text{-Bu})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{OMe})_2]$  [Al(1)–O(4) = 2.283 Å] [7]. This difference may be due to the lower steric bulk of the terminal alkoxide or to the changed electronic environment around the aluminum from  $\text{AlO}_3\text{C}_2$  to  $\text{AlO}_5$  or to a combination of both factors. The terminal ligand possesses 'slinky' type disorder [25] of the C–C–O–C chain, see Section 4.

Based on the above observations, it can be seen that the reactions of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  with the bifunctional potentially chelating alcohols,  $\text{HOCH}_2\text{CH}_2\text{EMe}_x$  ( $\text{E} = \text{O}, \text{S}, x = 1$ ;  $\text{E} = \text{N}, x = 2$ ), proceed as shown in Scheme 1. The initial reaction involves the protonolysis of the BHT ligand in preference to the hydride. The elimination of the BHT-H rather than hydrogen is presumably due to the greater basicity of the aryloxide oxygen than the aluminum hydride. We have observed similar decreases in basicity of aluminum alkyls in the presence of oxygen donor ligands [26]. The resulting mono-BHT compound dimerizes through the available

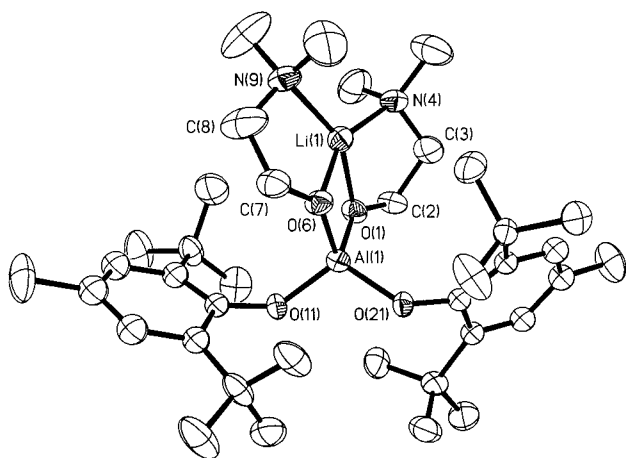


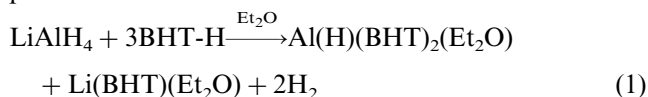
Fig. 3. Molecular structure of  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Li}$  (**8**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

alkoxide oxygen to give  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  (**2–4**). Reaction with further equivalents of  $\text{HOCH}_2\text{CH}_2\text{EMe}_x$  results in hydrogen elimination, forming  $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{EMe}_x)(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  (**5–7**). This reaction scheme is stoichiometrically controlled because in the presence of excess  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ , only  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$  (**2–4**) is formed.

Unfortunately, in all cases, the presence of only a single BHT does not preclude the formation of a dimer as we had hoped. In order to provide sufficient steric bulk to form a monomer containing potentially a bridging anionic oxygen, two BHT groups are needed [12]. To overcome this problem and to produce the potential latent Lewis acid,  $[(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)]_2$ ,  $\text{Al}(\text{BHT})_3$  was used as the starting material. Unfortunately, the results of the reactions of  $\text{Al}(\text{BHT})_3$  with  $\text{HOCH}_2\text{CH}_2\text{-EMe}_x$  were inconclusive by NMR spectroscopy.

### 2.1. Lithium aluminates

Traditionally,  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  has been synthesized from the reaction of  $\text{LiAlH}_4$  with BHT-H [15,16]. The lithium side product,  $\text{Li}(\text{BHT})(\text{Et}_2\text{O})$  (Eq. (1)) can be separated by multiple recrystallization steps. However, we have found that it is extremely difficult to separate the lithium salt completely from the desired product.



Because this was not previously an issue [15,16], our initial synthetic attempt to prepare  $(\text{BHT})_2\text{Al}(\text{OCH}_2\text{CH}_2\text{EMe}_x)$  using the product from Eq. (1) resulted in the isolation of a series of lithium aluminates.

If the reaction mixture formed from the reaction between  $\text{LiAlH}_4$  and BHT-H is reacted with  $\text{HO}$

$(\text{CH}_2)_2\text{EMe}_x$  ( $\text{E} = \text{O}, \text{S}, x = 1$ ;  $\text{E} = \text{N}, x = 2$ ), then the only isolable compounds are the lithium aluminates,  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{EMe}_x)_2\text{Li}$ . Compounds  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Li}$  (**8**),  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{-OMe})_2\text{Li}$  (**9**),  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}$  (**10**) have all been isolated and the presence of lithium in each was confirmed by a standard flame test. In addition, where an excess of  $\text{HO}(\text{CH}_2)_2\text{SMe}$  is employed the solvate,  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}\cdot(\text{HOCH}_2\text{CH}_2\text{SMe})$  (**11**), was also isolated in low yield. The monomeric structures of compounds **8–10** were verified by mass spectroscopy which showed peaks due to  $\text{M}^+$  and  $\text{M}^+ - \text{BHT}$  and the structures of these compounds are verified by the X-ray molecular structures of compounds **8** and the solvate of **11**.

The molecular structures of  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Li}$  (**8**) and  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}$  (**11**) are shown in Figs. 3 and 4, respectively; selected bond lengths and angles are given in Tables 3 and 4. Compounds **8** and **11** form monomeric structures with

Table 3  
Selected bond lengths (Å) and angles (°) for  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)_2\text{Li}$  (**8**)

Bond lengths			
Al(1)–O(1)	1.730(5)	Al(1)–O(21)	1.741(5)
Al(1)–O(11)	1.735(5)	Li(1)–O(1)	1.970(4)
Al(1)–O(6)	1.736(5)	Li(1)–O(6)	1.980(3)
Li(1)–N(4)	2.130(5)	Li(1)–N(9)	2.150(5)
Bond angles			
O(11)–Al(1)–O(21)	109.4(2)	O(11)–Al(1)–O(1)	117.0(2)
O(1)–Al(1)–O(6)	92.1(2)	O(11)–Al(1)–O(6)	110.3(2)
O(1)–Al(1)–N(9)	153.4(7)	O(1)–Al(1)–O(21)	110.3(2)
O(1)–Li(1)–O(6)	78.8(5)	O(6)–Li(1)–N(4)	154.3(7)
O(1)–Li(1)–N(4)	84.1(5)	O(6)–Li(1)–N(9)	84.5(5)
N(4)–Li(1)–N(9)	117.7(6)		

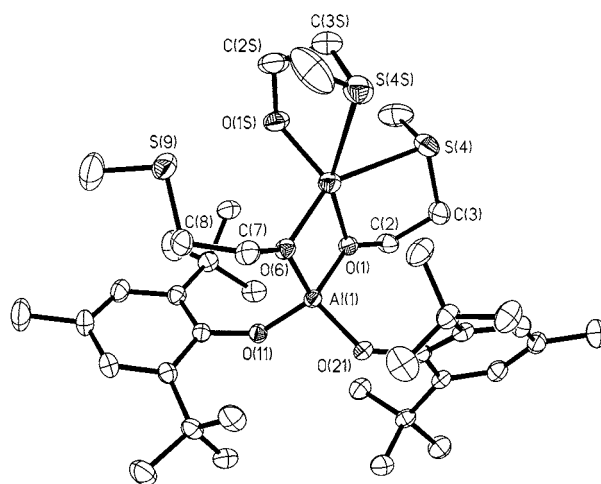


Fig. 4. Molecular structure of  $(\text{BHT})_2\text{Al}(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2\text{Li}(\text{HOCH}_2\text{CH}_2\text{SMe})$  (**11**). Thermal ellipsoids are shown at the 30% level and hydrogen atoms are omitted for clarity.

Table 4

Selected bond lengths (Å) and angles (°) for (BHT)<sub>2</sub>Al(μ-OCH<sub>2</sub>-CH<sub>2</sub>SMe)<sub>2</sub>Li(HOCH<sub>2</sub>CH<sub>2</sub>SMe) (**11**)

Bond lengths			
Al(1)–O(1)	1.747(3)	Al(1)–O(21)	1.746(2)
Al(1)–O(11)	1.736(3)	Li(1)–O(1)	1.982(8)
Al(1)–O(6)	1.753(3)	Li(1)–O(6)	2.004(7)
Li(1)–O(1S)	1.932(8)		
Bond angles			
O(11)–Al(1)–O(21)	106.6(1)	O(11)–Al(1)–O(1)	120.5(1)
O(1)–Al(1)–O(6)	90.7(1)	O(11)–Al(1)–O(6)	110.7(1)
O(1)–Al(1)–O(21)	108.7(1)	O(1)–Li(1)–O(6)	77.3(3)
O(6)–Li(1)–O(1S)	108.7(4)	O(1)–Li(1)–O(1S)	128.1(5)

a central AlO<sub>2</sub>Li core. The coordination geometry around the lithium atom is approximately tetrahedral in compound **8**, but it is more distorted than that around the aluminum due to the constraint of the four membered AlO<sub>2</sub>Li cycle and large N(4)–Li(1)–N(9) angle (117.7°). In compound **11**, the presence of the ligand adduct on lithium changes the geometry around the lithium and it becomes five-coordinate, distorted trigonal bipyramidal (see Fig. 4). Although X-ray data were collected for compounds **9** and **10**, their structures could not be refined to satisfactory values and the lithium atoms were not located. However the geometry of the ligands indicates that they are iso-structural to compound **8**. Other spectroscopic methods such as NMR spectroscopy and mass spectrometry support this claim.

Several lithium aluminates may be found in the literature, most of which exhibit a similar AlO<sub>2</sub>Li core [14,19,27,28]. In these cases; however, the lithium is coordinated to either the ether or THF molecules and this results in a three-coordinate, distorted trigonal planar arrangement. A tetrahedral geometry for lithium is seen in the dimer [(salpanAl)(Li(THF))<sub>2</sub>]<sub>2</sub> made by Atwood et al. [29] but the ligand attached to the lithium was not chelating, consequently, the geometry about the lithium was not as distorted as seen in compounds **8** and **11**. In compound LiAl[OC(Ph)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> [30], the AlO<sub>2</sub>Li core is similar to those seen in the other lithium aluminates, but the lithium is actually chelated by CF<sub>3</sub> substituents on the ligand and the geometry about the lithium atom becomes highly distorted. The geometry is uniquely six-coordinate and distorted from octahedral to trigonal prismatic. As in compounds **8** and **11**, the presence of the lithium atom stabilizes the monomer in this fluorinated compound. The lithium aluminates **8**, **11** and LiAl[OC(Ph)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> [21], may be considered as aluminum anions, chelating the lithium or as neutral covalent compounds.

The lithium cation is stabilized in the structure by formation of bonds with both the anionic oxygens as well as the neutral donor ligands. Bond valence theory describes the valence of atoms in a molecule and offers the ability to measure their bonding potential, i.e. it infers

Table 5

Bond valences<sup>a</sup> for the lithium bonds in (BHT)<sub>2</sub>Al(μ-OCH<sub>2</sub>CH<sub>2</sub>-NMe<sub>2</sub>)<sub>2</sub>Li (**8**) and (BHT)<sub>2</sub>Al(μ-OCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>Li·HOCH<sub>2</sub>CH<sub>2</sub>SMe (**11**)

<b>8</b>	<i>s</i>	<b>11</b>	<i>s</i>
Li(1)–O(1)	0.246	Li(1)–O(1)	0.238
Li(1)–O(6)	0.245	Li(1)–O(6)	0.227
Li(1)–N(9)	≈0.254	Li(1)–O(1S)	0.264
Li(1)–N(4)	≈0.254	Li(1)–S(4S)	≈0.14
		Li(1)–S(4)	≈0.14
Al(1)–O(1)	0.798	Al(1)–O(1)	0.763
Al(1)–O(6)	0.785	Al(1)–O(6)	0.751
Al(1)–O(11)	0.787	Al(1)–O(11)	0.785
Al(1)–O(21)	0.775	Al(1)–O(21)	0.765

<sup>a</sup> Bond valences were calculated from Eq. (2) where for Li–O bonds,  $R_0 = 1.292$ ,  $B = 0.48$  and for Al–O bonds,  $R_0 = 1.644$ ,  $B = 0.38$  [24].

the extent to which each bond contributes to the stability of an atom or ion and the sum of the bond valences at each atom is equal to the atomic valence [31,32]. Each bond valence may be calculated from Eq. (2), where  $s$  is the bond valence,  $R$  is the experimentally determined bond length, and  $R_0$  (the length of a bond of unit valence) and  $B$  are empirically determined parameters and can be found in the literature [24].

$$s = 10^{[-(R - R_0)/B]} \quad (2)$$

The calculated bond valences for the bonds to lithium and aluminum for compounds **8** and **11** are presented in Table 5. In both compounds the aluminum is nearly equally stabilized by all four oxygen donors. This is in accord with the theories that Haaland has postulated [33]. In compound **8**, the lithium is stabilized as much as, if not slightly more by the nitrogen atoms than the oxygen atoms. This may be due to the fact that the oxygens are also bonded to aluminum. In the case of compound **11**, the stabilization of the lithium is primarily by the oxygens as the sulfur donors contribute only 13.6% to the overall stability. This is obviously due to the weak association that the sulfur atoms have with the lithium and the fact that sulfur is a much softer base than oxygen. In the case of LiAl[OC(Ph)(CF<sub>3</sub>)<sub>2</sub>]<sub>4</sub> [22], the lithium atom is stabilized far more by the fluorines causing the C–F bonds to weaken [21].

### 3. Conclusions

These studies have shown that the reaction of (BHT)<sub>2</sub>Al(H)(Et<sub>2</sub>O) with bifunctional alcohols, HOCH<sub>2</sub>CH<sub>2</sub>ER'<sub>x</sub>, produces species that dimerize through the anionic oxygen on the ligands. The formation of the bis-aryloxide compounds is precluded due to the prefer-

ential elimination of the BHT ligand over the hydride. The formation of dimeric rather than monomeric structures is presumably due to the inability of only one BHT ligand to overcome the energy barrier present in the formation of a monomeric structure. Monomeric compounds could be synthesized as lithium aluminates formed from starting material that was made using  $\text{LiAlH}_4$ . These compounds show that the presence of a lithium atom stabilizes the monomeric bis-aryloxide compounds.

#### 4. Experimental

Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer operating with an electron beam energy of 70 eV for EI mass spectra. IR spectra (4000–400  $\text{cm}^{-1}$ ) were obtained using a Nicolet 760 FTIR infrared spectrometer. IR samples were prepared as Nujol mulls between KBr plates unless otherwise stated. NMR spectra were obtained on Bruker AM-250, spectrometer using (unless otherwise stated) benzene- $d_6$  solutions. Chemical shifts are reported relative to internal solvent resonances ( $^1\text{H}$  and  $^{13}\text{C}$ ).  $\text{HOCH}_2\text{CH}_2\text{OMe}$ ,  $\text{HOCH}_2\text{CH}_2\text{NMe}_2$  and  $\text{HOCH}_2\text{CH}_2\text{SMe}$  were obtained from Aldrich and were used after distillation.  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  was prepared as in the literature [15,16] and also prepared by substituting  $\text{LiAlH}_4$  with  $\text{NaAlH}_4$ .

##### 4.1. Reaction of $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ and $\text{HOCH}_2\text{CH}_2\text{NMe}_2$ (3:1)

To a solution of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  (1.50 g, 2.8 mmol) in  $\text{CH}_2\text{Cl}_2$  (50 ml) was added  $\text{HOCH}_2\text{CH}_2\text{NMe}_2$  (0.08 g, 0.93 mmol) dropwise. The mixture was allowed to stir overnight, after which time all volatiles were removed under vacuum and the residue was characterized by  $^1\text{H}$ -NMR spectroscopy. The  $^1\text{H}$ -NMR spectrum showed a mixture of BHT-H,  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ , excess  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  and  $[(\text{BHT})_2\text{Al}(\text{H})]_2$ . The mixture was then recrystallized from dichloromethane to give very few colorless crystals of  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ . The supernatant was then placed in the freezer and another crop of colorless crystals were isolated and characterized as  $[(\text{BHT})_2\text{Al}(\text{H})]_2$ .

##### 4.2. $[(\text{BHT})_2\text{Al}(\text{H})]_2$ (1)

M.p. 233–234°C. MS (EI, %):  $m/z$  698 ( $2\text{M}^+ - \text{BHT-Me}$ , 15), 451 ( $\text{M}^+ - \text{Me}$ , 25), 205 (BHT-H-Me, 100). IR ( $\text{cm}^{-1}$ ): 2740 (w), 1741 (m), 1393 (s), 1265 (s), 942 (s), 901 (s), 871(m), 778 (m), 640 (m).  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.11 [8H, s, m-CH], 4.26 [2H, s, Al-H], 2.20 [12H, s,  $\text{CH}_3$ ], 1.46 [72H, s,  $\text{C}(\text{CH}_3)_3$ ].  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  152.6 (CO), 127.0 (CH), 35.5 [ $\text{C}(\text{CH}_3)_3$ ], 32.3 [ $\text{C}(\text{CH}_3)_3$ ], 21.7 ( $\text{CH}_3\text{Ar}$ ).

##### 4.3. $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (2)

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.22 [4H, s, m-CH], 4.26 [2H, s, AlH], 3.71 [4H, t,  $J(\text{H-H}) = 5.7$  Hz,  $\text{OCH}_2$ ], 2.36 [4H, t,  $J(\text{H-H}) = 5.7$  Hz,  $\text{CH}_2\text{N}$ ], 2.30 [6H, s,  $\text{CH}_3$ ], 1.36 [12H, s,  $\text{N}(\text{CH}_3)_2$ ], 1.53 [36H, s,  $\text{C}(\text{CH}_3)_3$ ].

##### 4.4. Reaction of $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ and $\text{HOCH}_2\text{CH}_2\text{OMe}$ (3:1)

To a solution of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  (1.50 g, 2.8 mmol) in dichloromethane (50 ml) was added  $\text{HOCH}_2\text{CH}_2\text{OMe}$  (0.07 g, 0.93 mmol) dropwise at room temperature (r.t.). The mixture was allowed to stir overnight, filtered, and then the volatiles were removed from the filtrate in vacuo. The resultant solid was then characterized by  $^1\text{H}$ -NMR spectroscopy which showed a mixture of  $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ , BHT-H,  $[(\text{BHT})_2\text{Al}(\text{H})]_2$ , and excess  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ .

##### 4.5. $[(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{OMe})]_2$ (3)

$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.20 [4H, s, m-CH], 4.26 [2H, s, Al-H], 3.64 [4H, t,  $J(\text{H-H}) = 6.0$  Hz,  $\text{OCH}_2$ ], 3.10 [4H, t,  $J(\text{H-H}) = 6.0$  Hz,  $\text{CH}_2\text{O}$ ], 3.11 [6H, s,  $\text{OCH}_3$ ], 2.42 [6H, s,  $\text{CH}_3$ ], 1.59 [36H, s,  $\text{C}(\text{CH}_3)_3$ ].

##### 4.6. Reaction of $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ and $\text{HOCH}_2\text{CH}_2\text{SMe}$ (3:1)

To a solution of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  (2.0 g, 3.7 mmol) in dichloromethane (50 ml) was added  $\text{HOCH}_2\text{CH}_2\text{SMe}$  (0.11 g, 1.2 mmol) dropwise at r.t. The mixture was allowed to stir overnight, filtered, and the filtrate reduced to dryness in vacuo. The resultant solid was then characterized by  $^1\text{H}$ -NMR spectroscopy which showed a mixture of the following compounds:  $(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2$ , BHT-H,  $[(\text{BHT})_2\text{Al}(\text{H})]_2$  and excess  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$ .

##### 4.7. $(\text{BHT})\text{Al}(\text{H})(\mu\text{-OCH}_2\text{CH}_2\text{SMe})_2$ (4)

M.p. 115–117°C. IR ( $\text{cm}^{-1}$ ): 1828 (w,  $\nu_{\text{Al-H}}$ ), 1250 (s), 1116 (m), 886 (m), 871 (m), 666 (w), 625 (w).  $^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.19 [4H, s, m-CH], 3.53 [4H, t,  $J(\text{H-H}) = 5.4$  Hz,  $\text{OCH}_2$ ], 2.36 [6H, s,  $\text{OCH}_3$ ], 1.92 [4H, t,  $J(\text{H-H}) = 5.4$  Hz,  $\text{CH}_2\text{O}$ ], 1.72 [36H, s,  $\text{C}(\text{CH}_3)_3$ ], 1.35 [6H, s,  $\text{CH}_3$ ].  $^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  139.7 (CO), 126.5 (CH), 36.1 ( $\text{SCH}_2$ ), 32.4 [ $\text{C}(\text{CH}_3)_3$ ], 30.8 [ $\text{C}(\text{CH}_3)_3$ ], 21.7 ( $\text{CH}_3\text{Ar}$ ), 12.9 ( $\text{SCH}_3$ )

##### 4.8. $[(\text{BHT})\text{Al}(\text{OCH}_2\text{CH}_2\text{NMe}_2)(\mu\text{-OCH}_2\text{CH}_2\text{NMe}_2)]_2$ (5)

To a solution of  $(\text{BHT})_2\text{Al}(\text{H})(\text{Et}_2\text{O})$  (1.15 g, 2.1 mmol) in dichloromethane (50 ml) was added  $\text{HOCH}_2\text{CH}_2\text{NMe}_2$  (0.19 g, 2.1 mmol) dropwise at r.t. The mixture was

allowed to stir overnight, filtered, and the filtrate was placed in the freezer for crystallization. A few colorless crystals were isolated and were insufficient for complete characterization.  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  6.94 [4H, s, m-CH], 3.28 [4H, t,  $J(\text{H-H}) = 5.1$  Hz,  $\text{OCH}_2$ ], 2.13 [6H, s,  $\text{CH}_3$ ], 1.86 [8H, t,  $J(\text{H-H}) = 5.1$  Hz,  $\text{CH}_2\text{N}$ ], 1.68 [24H, s,  $\text{N}(\text{CH}_3)_2$ ] 1.34 [36H, s,  $\text{C}(\text{CH}_3)_3$ ].

#### 4.9. [(BHT)Al(OCH<sub>2</sub>CH<sub>2</sub>OMe)( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>OMe)]<sub>2</sub> (6)

To a solution of (BHT)<sub>2</sub>Al(H)(Et<sub>2</sub>O) (1.75 g, 3.2 mmol) in dichloromethane (50 ml) was added HOCH<sub>2</sub>CH<sub>2</sub>OMe (0.25 g, 3.2 mmol) in a dropwise manner at r.t. The mixture was allowed to stir overnight, filtered, and the filtrate was placed in the freezer for crystallization. Colorless crystals then precipitated. Yield: ca. 10%. M.p. 163–166°C. MS (EI, %):  $m/z$  573 (2M<sup>+</sup> – BHT, 100), 396 (M<sup>+</sup>, 15), 353 (2M<sup>+</sup> – 2 BHT-H, 10), 205 (BHT-H-Me, 15). IR (cm<sup>-1</sup>): 2719 (w), 1265 (m), 1157 (w), 1050 (m, br), 927 (w), 866 (w), 804 (w), 722 (w), 666 (w).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.28 [4H, s, m-CH], 3.66 [4H, t,  $J(\text{H-H}) = 4.6$  Hz,  $\text{OCH}_2$ ], 3.34 [4H,  $J(\text{H-H}) = 4.2$  Hz,  $\text{OCH}_2$ ], 2.98 [4H, t,  $J(\text{H-H}) = 4.6$  Hz,  $\text{CH}_2\text{O}$ ], 2.94 [6H, s,  $\text{ArCH}_3$ ], 2.80 [4H,  $J(\text{H-H}) = 4.2$  Hz,  $\text{OCH}_2$ ], 2.73 [6H, s,  $\text{OCH}_3$ ], 2.39 [6H, s,  $\text{OCH}_3$ ], 1.82 [36H, s,  $\text{C}(\text{CH}_3)_3$ ].

#### 4.10. Reaction of (BHT)<sub>2</sub>Al(H)(Et<sub>2</sub>O) and HO(CH<sub>2</sub>)<sub>2</sub>SMe (1:1)

To a solution of (BHT)<sub>2</sub>Al(H)(Et<sub>2</sub>O) (1.50 g, 2.8 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was added HO(CH<sub>2</sub>)<sub>2</sub>SMe (0.26 g, 2.8 mmol) in a dropwise manner at r.t. The mixture was allowed to stir overnight and reduced to dryness in vacuo.  $^1\text{H-NMR}$  spectroscopy revealed a mixture of [(BHT)Al(OCH<sub>2</sub>CH<sub>2</sub>SMe)( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>SMe)]<sub>2</sub>, BHT-H and compound **3**. Compound **3** was isolated as residue by washing the mixture with pentane.

#### 4.11. [(BHT)Al(OCH<sub>2</sub>CH<sub>2</sub>SMe)( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>SMe)]<sub>2</sub> (7)

$^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.25 [4H, s, m-CH, 3.73 [8H, t,  $J(\text{H-H}) = 7.0$  Hz,  $\text{OCH}_2$ ], 2.33 [6H, s,  $\text{CH}_3$ ], 1.99 [8H, t,  $J(\text{H-H}) = 7.0$  Hz,  $\text{CH}_2\text{S}$ ], 1.68 [36H, s,  $\text{C}(\text{CH}_3)_3$ ] 1.38 [6H, s,  $\text{SCH}_3$ ].

#### 4.12. (BHT)<sub>2</sub>Al( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>Li (8)

To a mixture of Li(BHT)(OEt<sub>2</sub>) and (BHT)<sub>2</sub>Al(H)-(Et<sub>2</sub>O) (1.5 g, 2.8 mmol) dissolved in hexane (50 ml) was added HOCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> (0.25 g, 2.8 mmol). The mixture was allowed to stir overnight, filtered and the filtrate placed at –22°C from whence colorless crystals precipitated. Yield: 80%. M.p. 152–154°C. MS (EI, %):  $m/z$  648 (M<sup>+</sup>, 5), 429 (M<sup>+</sup> – BHT, 100), 341 (M<sup>+</sup> – BHT-OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>, 40). IR (cm<sup>-1</sup>): 1829 (w), 1262

(s), 1163 (w), 1116 (m), 1026 (m), 945 (w), 898 (w), 870 (w), 804 (m), 780 (w), 719 (m).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.26 [4H, s, m-CH], 3.54 [4H, t,  $J(\text{H-H}) = 5.3$  Hz,  $\text{OCH}_2$ ], 2.36 [6H, s,  $\text{ArCH}_3$ ], 1.78 [4H, t,  $J(\text{H-H}) = 5.3$  Hz,  $\text{CH}_2\text{N}$ ], 1.73 [36H, s,  $\text{C}(\text{CH}_3)_3$ ], 1.61 [12H, s,  $\text{N}(\text{CH}_3)_2$ ].  $^{27}\text{Al-NMR}$  ( $\text{C}_7\text{H}_8$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  43 ( $W_{1/2} = 897$  Hz).

#### 4.13. (BHT)<sub>2</sub>Al( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>OMe)<sub>2</sub>Li (9)

To a mixture of Li(BHT)(OEt<sub>2</sub>) and (BHT)<sub>2</sub>Al(H)-(Et<sub>2</sub>O) (1.5 g, 2.8 mmol) dissolved in hexane (50 ml), was added HOCH<sub>2</sub>CH<sub>2</sub>OMe (0.21 g, 2.8 mmol). The mixture was allowed to stir overnight, filtered and the filtrate was placed at –22°C from which colorless crystals precipitated. Yield: 81%. M.p. 74–75°C. MS (EI, %):  $m/z$  622 (M<sup>+</sup>, 10), 547 (M<sup>+</sup> – OCH<sub>2</sub>CH<sub>2</sub>OMe, 5), 403 (M<sup>+</sup> – BHT, 100). IR (cm<sup>-1</sup>): 2730 (w), 1378 (s), 1265 (m), 1157 (w), 1091 (m), 932 (w), 860 (w), 799 (m), 722 (m), 482 (s).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.28 [4H, s, m-CH], 3.62 [4H, t,  $J(\text{H-H}) = 4.8$  Hz,  $\text{OCH}_2$ ], 2.80 [4H, t,  $J(\text{H-H}) = 4.8$  Hz,  $\text{CH}_2\text{O}$ ], 2.62 [6H, s,  $\text{OCH}_3$ ], 2.37 [6H, s,  $\text{ArCH}_3$ ], 1.73 [36H, s,  $\text{C}(\text{CH}_3)_3$ ].  $^{27}\text{Al-NMR}$  ( $\text{C}_7\text{H}_8$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  44 ( $W_{1/2} = 996$  Hz).

#### 4.14. (BHT)<sub>2</sub>Al( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>Li (10)

To a mixture of Li(BHT)(OEt<sub>2</sub>) and (BHT)<sub>2</sub>Al(H)-(Et<sub>2</sub>O) (1.5 g, 2.8 mmol) dissolved in hexane (50 ml), was added HO(CH<sub>2</sub>)<sub>2</sub>SMe (0.26 g, 2.8 mmol). The mixture was allowed to stir overnight, filtered and the filtrate was placed at –22°C from which colorless crystals precipitated. Yield: 78%. M.p. 189–190°C. MS (EI, %):  $m/z$  654 (M<sup>+</sup>, 10), 435 (M<sup>+</sup> – BHT, 100), 344 (M<sup>+</sup> – BHT-OCH<sub>2</sub>CH<sub>2</sub>SMe, 10), 205 (BHT-Me, 65). IR (cm<sup>-1</sup>): 2719 (w), 1285 (w), 1234 (m), 1198 (w), 1111 (m), 855 (m), 804 (w), 784 (m), 722 (w), 661 (m).  $^1\text{H-NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.20 [4H, s, m-CH], 3.51 [4H, t,  $J(\text{H-H}) = 5.1$  Hz,  $\text{OCH}_2$ ], 2.32 [6H, s,  $\text{CH}_3$ ], 1.97 [4H, t,  $J(\text{H-H}) = 5.1$  Hz,  $\text{CH}_2\text{S}$ ], 1.70 [36H, s,  $\text{C}(\text{CH}_3)_3$ ], 1.36 [6H, s,  $\text{SCH}_3$ ].  $^{27}\text{Al-NMR}$  ( $\text{C}_7\text{H}_8$ ,  $\text{C}_6\text{D}_6$ ):  $\delta$  50 ( $W_{1/2} = 1744$  Hz).

Where an excess of HO(CH<sub>2</sub>)<sub>2</sub>SMe was employed the solvate, (BHT)<sub>2</sub>Al( $\mu$ -OCH<sub>2</sub>CH<sub>2</sub>SMe)<sub>2</sub>Li(HOCH<sub>2</sub>CH<sub>2</sub>-SMe) (**11**), was also isolated in low yield.

## 5. Crystallographic studies

Crystals of compounds **2**, **6**, **8**, and **11** were sealed in a glass capillary under argon and mounted on the goniometer of a Rigaku AFC-5S automated diffractometer (**8** and **11**) or a Bruker CCD Smart System diffractometer (**2** and **6**). Data collection and cell determinations were performed in a manner previously described [34]. The locations of the majority of non-hydrogen atoms were obtained by using SHELXTL [35].

Table 6  
Summary of X-ray diffraction data

Compound	[(BHT)Al(H)- ( $\mu$ -OCH <sub>2</sub> CH <sub>2</sub> NMe <sub>2</sub> ) <sub>2</sub> ] <sub>2</sub> ( <b>2</b> ) 2CH <sub>2</sub> Cl <sub>2</sub>	[(BHT)Al(OCH <sub>2</sub> CH <sub>2</sub> OMe)- ( $\mu$ -OCH <sub>2</sub> CH <sub>2</sub> OMe) <sub>2</sub> ] <sub>2</sub> ( <b>6</b> ) 2CH <sub>2</sub> Cl <sub>2</sub>	(BHT) <sub>2</sub> Al( $\mu$ -OCH <sub>2</sub> CH <sub>2</sub> - NMe <sub>2</sub> ) <sub>2</sub> Li ( <b>8</b> )	(BHT) <sub>2</sub> Al( $\mu$ -OCH <sub>2</sub> CH <sub>2</sub> SMe) <sub>2</sub> - Li(HOCH <sub>2</sub> CH <sub>2</sub> SMe) ( <b>11</b> )
Empirical formula	C <sub>40</sub> H <sub>72</sub> Al <sub>2</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>4</sub>	C <sub>44</sub> H <sub>78</sub> Al <sub>2</sub> Cl <sub>4</sub> O <sub>10</sub>	C <sub>38</sub> H <sub>66</sub> AlLiN <sub>2</sub> O <sub>4</sub>	C <sub>39</sub> H <sub>68</sub> AlLiO <sub>5</sub> S <sub>3</sub>
Crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>Pbcn</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	12.002(2)	8.622(2)	18.039(4)	15.451(3)
<i>b</i> (Å)	15.805(3)	11.135(2)	20.915(4)	13.711(3)
<i>c</i> (Å)	12.936(3)	14.351(3)	21.918(4)	11.409(2)
$\alpha$ (°)		70.83(3)		96.03(3)
$\beta$ (°)	105.41(3)	86.67(3)		106.10(3)
$\gamma$ (°)		87.86(3)		101.32(3)
<i>V</i> (Å <sup>3</sup> )	2365.6(8)	1298.9(4)	8269(3)	2244.1(8)
<i>Z</i>	2	1	8	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.18	1.231	1.042	1.106
$\mu$ (cm <sup>-1</sup> )	0.33	0.31	0.085	0.22
Temperature (K)	293	293	293	293
2 $\theta$ Range (°)	4–45	4.0–45.0	4–55	4–45
Reflections collected	3258	3608	5915	5713
Independent reflections	3088	3396	5915	5451
Reflections observed	2024	2261	2046	3763
Weighting scheme	( $ F_o  > 4.0\sigma F_o $ ) $w^{-1} = 0.04( F_o )^2 + \sigma( F_o )^2$	( $ F_o  > 4.0\sigma F_o $ ) $w^{-1} = 0.04( F_o )^2 + \sigma( F_o )^2$	( $ F_o  > 4.0\sigma F_o $ ) $w^{-1} = 0.04( F_o )^2 + \sigma( F_o )^2$	( $ F_o  > 4.0\sigma F_o $ ) $w^{-1} = 0.04( F_o )^2 + \sigma( F_o )^2$
<i>R</i>	0.0587	0.062	0.082	0.054
<i>R</i> <sub>w</sub>	0.147	0.165	0.181	0.147
Largest difference peak and hole (e Å <sup>-3</sup> )	0.45/–0.40	0.41/–0.33	0.26/–0.34	0.47/–0.32

The terminal ligand possesses 'slinky' type disorder [36] of the C–C–O–C chain and the solvent molecule, CH<sub>2</sub>Cl<sub>2</sub>, located within the unit cell, demonstrates rotational disorder such that four Cl positions were observed. All Al hydrides were refined freely, and all other hydrogen atoms were included with fixed thermal parameters and constrained to 'ride' upon the appropriate atoms [*d*(C–H) = 0.95 Å]. A summary of cell parameters, data collection, and structure solution is given in Table 6. Scattering factors were taken from Ref. [37].

## 6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 134139 for compound **2**, 134140 for compound **6**, 134141 for compound **8**, and 134138 for compound **11**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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