

Aluminum Complexes with Sulfide-Linked Bis(phenolato) Ligands: Unusual Structure and Reactivity of the Methyl Bis(phenolato) Complex “[Al(tbmp)Me]” (tbmp = 2,2'-Thiobis(6-tert-butyl-4-methylphenolato))

Wigand Braune, Haiyan Ma, Thomas P. Spaniol, and Jun Okuda*

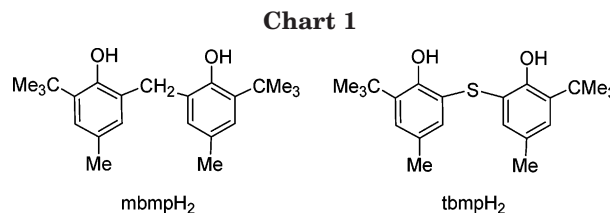
Institute of Inorganic Chemistry, RWTH Aachen University of Technology, Landoltweg 1, D-52056 Aachen, Germany

Received November 29, 2004

Trialkylaluminum complexes, AlR_3 (R = Me, Et), reacted with the sulfide-bridged bis(phenol) tbmpH_2 (tbmp = 2,2'-thiobis(6-tert-butyl-4-methylphenol)) in a 1:1 ratio to give monoalkyl compounds of the composition “[Al(tbmp)R]” with an unsymmetrical dinuclear structure with both six- and four-coordinate aluminum centers in the solid state. The reaction of 2 equiv of tbmpH_2 gave [Al(tbmp)(tbmpH)], which could be deprotonated with triethylamine to give $[\text{NEt}_3\text{H}][\text{Al}(\text{tbmp})_2]$. Upon reaction of [Al(tbmp)R]₂ with Lewis bases L (L = Et₂O, THF, propylene oxide), monomeric, five-coordinate adducts [Al(tbmp)R(L)] were formed, while 2-propanol gave the dinuclear complex [Al(tbmp)(μ-OⁱPr)]₂.

Introduction

Aluminum complexes of chelating O-donor ligands such as functionalized phenolato ligands exhibit a rich structural variety in both the crystalline and solution states. Currently there is considerable interest in employing structurally well-characterized aluminum complexes as efficient initiators for the ring-opening polymerization of heterocyclic monomers which include lactones,¹ lactides,² and, more recently, epoxides.³ In particular, aluminum complexes with easily available bis(phenolato) ligands such as the methylene-linked ligand mbmp (mbmp = 2,2'-methylenebis(6-tert-butyl-4-methylphenolato); Chart 1) have attracted some attention. The introduction of a sulfide instead of a methylene bridge has led to an enhanced polymerization activity for the titanium-based alkene polymerization



catalysts with linked bis(phenolato) ligands.^{4,5} It has been shown for sulfide-linked bis(phenolato) ligands such as tbmp (tbmp = 2,2'-thiobis(6-tert-butyl-4-methylphenolato))⁶ that the heteroatom donor interacts with the Lewis acidic metal center, leading to higher coordination numbers, but in a hemilabile fashion. As

(1) For reviews, see: (a) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215. (b) Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K. *J. Chem. Soc., Dalton Trans.* **2003**, 4039. (c) Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2003**, *242*, 97. For bis(phenolato) aluminum initiators, see: (d) Lin, C.-H.; Yan, L.-F.; Wang, F.-C.; Sun, Y.-L.; Lin, C.-C. *J. Organomet. Chem.* **1999**, *587*, 151. (e) Taden, I.; Kang, H.-C.; Massa, W.; Spaniol, T. P.; Okuda, J. *Eur. J. Inorg. Chem.* **2000**, *3*, 441. (f) Chen, H.-L.; Ko, B.-T.; Huang, B.-H.; Lin, C.-C. *Organometallics* **2001**, *20*, 5076. (g) Ko, B.-T.; Lin, C.-C. *Macromolecules* **1999**, *32*, 8296. (h) Ko, B.-T.; Wu, C.-C.; Lin, C.-C. *Organometallics* **2000**, *19*, 1864. (i) Ko, B.-T.; Chao, Y.-C.; Lin, C.-C. *Inorg. Chem.* **2000**, *39*, 1463. (j) Ko, B.-T.; Chao, Y.-C.; Lin, C.-C. *J. Organomet. Chem.* **2000**, *598*, 13. (k) Liu, Y.-C.; Ko, B.-T.; Lin, C.-C. *Macromolecules* **2001**, *34*, 6196. (l) Ziemkowska, W.; Kucharski, S.; Kolodziej, A.; Anulewicz-Ostrowska, R. *J. Organomet. Chem.* **2004**, *689*, 2930.

(2) For initiators for lactide polymerization based on Schiff base ligands, see: (a) Spassky, N.; Winiewsky, M.; Pluta, C.; Le Borgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627. (b) Radano, C. P.; Baker, G. L.; Smith, M. R., III. *J. Am. Chem. Soc.* **2000**, *122*, 1552. (c) Nomura, N.; Ishi, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (d) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316. (e) Zhong, Z.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291. For initiators for lactide polymerization based on other ligands, see: (f) Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382.

(3) (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Emig, N.; Nguyen, H.; Krautscheid, H.; Réau, R.; Cazaux, J.-B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599. (c) Braune, W.; Okuda, J. *Angew. Chem.* **2003**, *115*, 67; *Angew. Chem., Int. Ed.* **2003**, *43*, 65. (d) Chisholm, M. H.; Navarro-Llobet, D.; Simonsick, W. J., Jr. *Macromolecules* **2001**, *34*, 8851. (e) Antelmann, B.; Chisholm, M. H.; Iyer, S. S.; Huffman, J. C.; Navarro-Llobet, D.; Pagel, M.; Simonsick, W. J.; Zhong, W. *Macromolecules* **2001**, *34*, 3159. For review on coordinate PO polymerization, see: Sugimoto, S.; Inoue, S. *Adv. Polym. Sci.* **1999**, *146*, 39. Kuran, W. *Prog. Polym. Sci.* **1998**, *23*, 919.

(4) (a) Fokken, S.; Spaniol, T. P.; Kang, H.-C.; Massa, W.; Okuda, J. *Organometallics* **1996**, *15*, 5069. (b) Sernetz, F. G.; Müllhaupt, R.; Fokken, S.; Okuda, J. *Macromolecules* **1997**, *30*, 1562. (c) Okuda, J.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P. *Eur. J. Inorg. Chem.* **2000**, 1321. (d) Nakayama, Y.; Watanabe, K.; Ueyama, N.; Nakamura, A.; Harada, A.; Okuda, J. *Organometallics* **2000**, *19*, 2498. (e) Amor, F.; Fokken, S.; Kleinhenn, T.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2001**, *621*, 3. (f) Fokken, S.; Reichwald, F.; Spaniol, T. P.; Okuda, J. *J. Organomet. Chem.* **2002**, *663*, 158. (g) Natrajan, L. S.; Wilson, C.; Okuda, J.; Arnold, P. L. *Eur. J. Inorg. Chem.* **2004**, 3724.

(5) (a) Miyatake, T.; Mizunuma, K.; Seki, Y.; Kakugo, M. *Macromol. Chem., Rapid Commun.* **1989**, *10*, 349. Miyatake, T.; Mizunuma, K.; Kakugo, M. *Macromol. Chem., Macromol. Symp.* **1993**, *66*, 203. (b) van der Linden, A.; Schavariën, C. J.; N. Meijboom, N.; Ganter, C.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 3008. (c) Porri, L.; Ripa, A.; Colombo, P.; Miano, E.; Capelli, S.; Meille, S. V. *J. Organomet. Chem.* **1996**, *514*, 213. (d) Froese, R. D. J.; Musaev, D. G.; Matsubara, T.; Morokuma, K. *J. Am. Chem. Soc.* **1997**, *119*, 7190. Froese, R. D. J.; Musaev, D. G.; Morokuma, K. *Organometallics* **1999**, *18*, 373.

aluminum complexes with the tbmp ligand are still very rare in the literature,⁷ we have performed systematic studies on aluminum complexes containing a tbmp ligand as part of our effort to explore the coordination mode of this dianionic [OSO] ligand at hard Lewis acidic metal centers. We report here that the coordination behavior of the tbmp ligand at the aluminum center considerably differs from that of the mbmp ligand, underlining the importance of the aluminum–sulfur interaction.⁸

Results and Discussion

Trimethylaluminum reacted with 1 equiv of tbmpH₂ in hexane under methane evolution to give a single product of the composition “[Al(tbmp)Me]” (**1**) as a colorless powder in ca. 90% yield (Scheme 1). A crystal structure determination of **1** revealed an unsymmetrical dinuclear structure with markedly different ligand spheres for each of the two aluminum centers (Figure 1): one is octahedrally coordinated by two tbmp ligands (cis S,S), whereas the other is tetrahedrally coordinated by the two phenolic oxygen atoms of one tbmp ligand as well as by two terminal methyl groups. The Al–S bond interaction is negligible for the latter aluminum center (Al2–S2 = 3.764(3) Å). For the octahedrally coordinated aluminum, the Al–S bond lengths of 2.451(3) and 2.518(3) Å are relatively short but are within the range of other reported aluminum–thioether bond distances.^{7,8} It should be noted that aluminum–sulfur interactions can be rather variable (from 2.618(4) Å in [Al(CH₂SMe)₃]^{8k} up to 3.277 Å in [Me₂Al(μ-OCH₂-CH₂SMe)AlMe₃]₂^{8g} for coordination number 5; from 2.406(2) Å in [Al(μ-CH₂SPh)₃]₂^{8k} up to 2.718(3) Å in [Al(CH₃)₃][12]aneS₄^{8b} for coordination number 4). ¹H

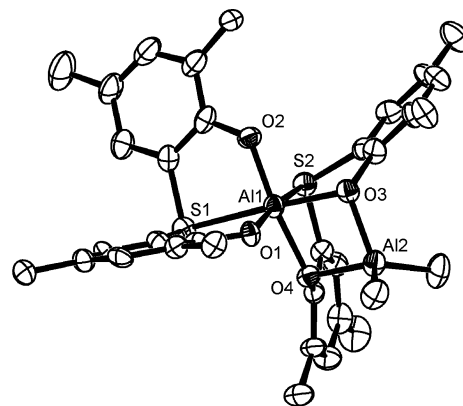
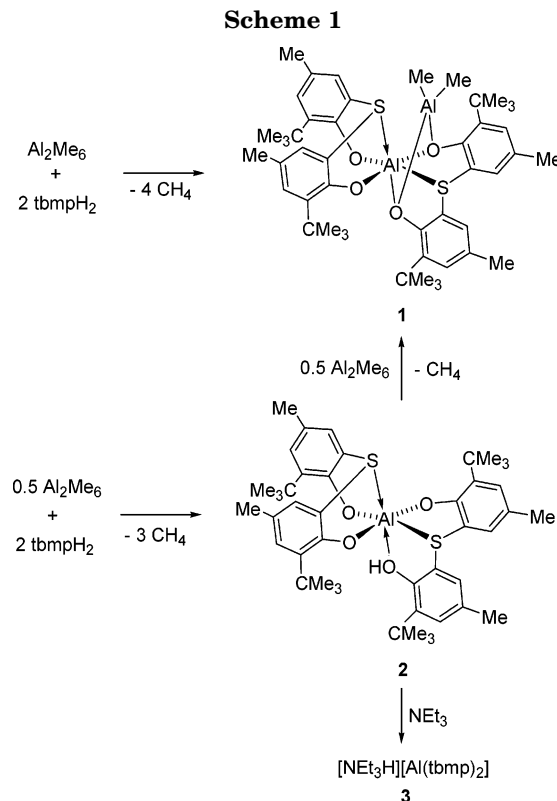


Figure 1. ORTEP diagram of the molecular structure of [Al(tbmp)Me]₂ (**1**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. For *tert*-butyl groups, only carbon atoms connected to phenyl ring are shown. Selected bond lengths (Å) and bond angles (deg): Al1–O1 = 1.772(5), Al1–O2 = 1.779(5), Al1–O3 = 1.895(5), Al1–O4 = 1.983(5), Al1–S1 = 2.451(3), Al1–S2 = 2.518(3), Al1–Al2 = 2.852(3), Al2–O3 = 1.878(6), Al2–O4 = 1.877(6), Al2–C45 = 1.930(9), Al2–C46 = 1.937(8); O3–Al1–S1 = 170.5(2), O1–Al1–S2 = 169.8(2), O2–Al1–O4 = 164.6(3), O1–Al1–O2 = 103.1(3), O1–Al1–O4 = 92.3(2), O3–Al2–O4 = 82.7(2), C45–Al2–C46 = 119.4(4).

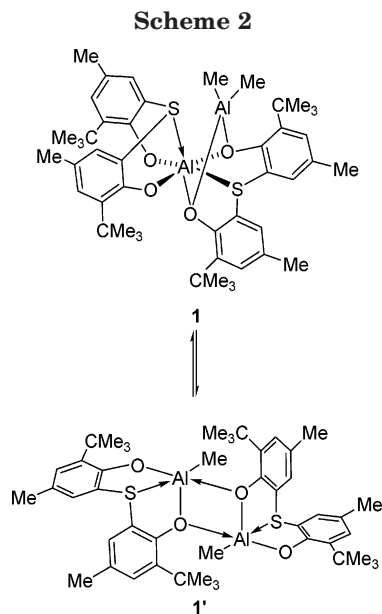
(6) For other metal complexes containing a tbmp or related ligands, see: (a) Pastor, S. D.; Prakasha, T. K.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 2690. (b) Paine, T. K.; Weyhermüller, T.; Slep, L. D.; Neese, F.; Bill, E.; Bothe, E.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **2004**, *43*, 7324. (c) Paine, T. K.; Weyhermüller, T.; Bothe, E.; Wieghardt, K.; Chaudhuri, P. *Dalton Trans.* **2003**, 3136. (d) Takashima, Y.; Nakayama, Y.; Yasuda, H.; Nakamura, A.; Harada, A. *J. Organomet. Chem.* **2002**, *664*, 234. (e) Paine, T. K.; Weyhermüller, T.; Wieghardt, K.; Chaudhuri, P. *Inorg. Chem.* **2002**, *41*, 6538. (f) Takashima, Y.; Nakayama, Y.; Watanabe, K.; Itono, T.; Ueyama, N.; Nakamura, A.; Yasuda, H.; Okuda, J. *Macromolecules* **2002**, *35*, 7538. (g) Takashima, Y.; Nakayama, Y.; Yasuda, H.; Harada, A. *J. Organomet. Chem.* **2002**, *651*, 114. (h) Arnold, P. L.; Natrajan, L. S.; Hall, J. J.; Bird, S. J.; Wilson, C. *J. Organomet. Chem.* **2002**, *647*, 205. (i) Chaudhuri, P.; Hess, M.; Florke, U.; Wieghardt, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 2217. (j) Pastor, S. D.; Huang, V.; NabiRahni, D.; Koch, S. A.; Hsu, H.-F. *Inorg. Chem.* **1997**, *36*, 5966.

(7) (a) Ohba, Y.; Ito, K.; Nagasawa, T.; Sakurai, S. *J. Heterocycl. Chem.* **2000**, *37*, 1071. (b) Doledec, G.; Commereuc, D. *J. Mol. Catal., A: Chem.* **2000**, *161*, 125. For examples with two thioether groups in the link, see: (c) Ma, H.; Melillo, G.; Oliva, L.; Spaniol, T. P.; Englert, U.; Okuda, J. *Dalton Trans.* **2005**, 721. Ma, H.; Melillo, G.; Oliva, L.; Spaniol, T. P.; Englert, U.; Okuda, J. *Acta Crystallogr., Sect. E* **2005**, *E61*, m221.

(8) For examples of complexes with Al–S(thioether) interactions, see: (a) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887. (b) Robinson, G. H.; Sangokoya, S. *J. Am. Chem. Soc.* **1988**, *110*, 1494. (c) Kumar, R.; de Mel, V. S.; Oliver, J. P. *Organometallics* **1989**, *8*, 2488. (d) Hendershot, D. G.; Barber, M.; Kumar, R.; Oliver, J. P. *Organometallics* **1991**, *10*, 3302. (e) Dickson, P. M.; Oliver, J. P. *Organometallics* **1994**, *13*, 3300. (f) Taghiof, M.; Heeg, J.; Bailey, M.; Dick, D. G.; Kumar, R.; Hendershot, D. G.; Rahbarnoohi, H.; Oliver, J. P. *Organometallics* **1995**, *14*, 2903. (g) Francis, J.; McMahon, C. N.; Bott, S. G.; Barron, A. R. *Organometallics* **1999**, *18*, 4399. (h) Janas, Z.; Jerykiewicz, L.; Przybylak, S.; Richards, R. L.; Sobota, P. *Organometallics* **2000**, *19*, 4252. (i) Lustig, C.; Mitzel, N. W. *Organometallics* **2002**, *21*, 3471. (j) Schumann, H.; Girgides, F.; Dechert, S.; Gottfriedsen, J.; Hummert, S.; Schütte, S.; Pickardt, J. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2625. (k) Rüffer, T.; Bruhn, C.; Rusanov, E.; Nordhoff, K.; Steinborn, D. *Z. Anorg. Allg. Chem.* **2002**, *628*, 421.



and ¹³C NMR spectroscopic measurements showed that the asymmetric structure of compound **1** is retained in solution at room temperature. ¹H NMR spectra at higher temperatures (C₆D₅Br, 25–100 °C) show broadening of all resonances and the appearance of a new set of signals, indicating the presence of the symmetrical complex **1'** (Scheme 2). We tentatively assume a structure for **1'** which is similar to that of the compound with a methylene instead of a sulfide bridge, [Al(mbmp)Me]₂ displaying a C_i-symmetrical structure with μ-oxygen



bonds with tetrahedrally coordinated aluminum atoms.⁹ The tetrahedrally coordinated AlMe_2 units are often encountered in polynuclear aluminum complexes derived from chelating ligands. Trimetallic aluminum complexes with tetraanionic $[\text{N}_2\text{O}_2]$ -type ligands reported by Atwood et al.¹⁰ contain two tetrahedral AlEt_2 fragments which are bonded across an $[\text{OO}]$ chelate part similar to that observed in **1**, although related dianionic $[\text{N}_2\text{O}_2]$ -type ligands were found to react with AlR_3 to give monomeric complexes.¹¹ Despite the unsymmetrical structure for **1**, as indicated by its ^1H NMR spectra, the ^{27}Al NMR spectra ($\text{CDCl}_3/\text{CD}_2\text{Cl}_2$) displayed only one very broad signal at 52 ppm ($w_{1/2} = 4878$ Hz). This chemical shift is within the range for five-coordinate aluminum centers according to literature reports.^{10a,b,12,13} When the temperature is lowered to -80 °C, this

(9) ^1H and ^{13}C NMR spectra of this compound were reported in ref 1e. Crystals of $[\text{Al}(\text{mbmp})\text{Me}_2]$ were obtained from a solution of CDCl_3 . A structure determination by X-ray diffraction gave the following parameters: $a = 16.609(1)$ Å, $b = 11.601(1)$ Å, $c = 27.793(3)$ Å, $\beta = 92.342(8)^\circ$, $V = 5350.7(8)$ Å³, tentative space group $C2/c$ (No. 15). The structure solution has established the molecular connectivity and symmetry. However, the crystal contains severely disordered CDCl_3 . The results of the refinement were unsatisfactory, and therefore, the data are not discussed.

(10) (a) Atwood, D. A.; Jegier, J. A.; Martin, K. J.; Rutherford, D. *Organometallics* **1995**, *14*, 1453. (b) Atwood, D. A.; Rutherford, D. *Organometallics* **1995**, *14*, 3988. (c) Atwood, D. A.; Remington, M. P.; Rutherford, D. *Organometallics* **1996**, *15*, 4763. For structurally related trimetallic complexes, see ref 1l. Zienkowska, W. *Polyhedron* **2002**, *21*, 281.

(11) (a) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688. (b) Tang, Z.; Chen, X.; Pang, X.; Yang, Y.; Zhang, X.; Jing, X. *Biomacromolecules* **2004**, *5*, 965. (c) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938. (d) Taden, I.; Kang, H.-C.; Massa, W.; Okuda, J. *J. Organomet. Chem.* **1997**, *540*, 189.

(12) (a) Lewiński, J.; Zachara, J.; Justyniak, I. *Organometallics* **1997**, *16*, 3859. (b) Paek, C.; Kang, S.-O.; Ko, J. *Organometallics* **1997**, *16*, 1503. (c) Fryzuk, M. D.; Giesbrecht, G. R.; Olovsson, G.; Rettig, S. J. *Organometallics* **1996**, *15*, 4832. (d) Passarelli, V.; Carta, G.; Rossetto, G.; Zanella, P. *Dalton Trans.* **2003**, 1284. (e) Lustig, C.; Mitzel, N. W. *Angew. Chem.* **2001**, *113*, 4521. (f) Szumacher, S.; Madura, I.; Zachara, J.; Kunicki, A. R.; Cebulski, A.; Jerzykiewicz, L. *J. Organomet. Chem.* **2003**, *669*, 64. (g) Wang, Z.-X.; Li, Y.-X. *Organometallics* **2003**, *22*, 4900. (h) Lustig, C.; Mitzel, N. W. *Organometallics* **2003**, *22*, 242. (i) Wrobel, O.; Schaper, F.; Wieser, U.; Gregorius, H.; Brintzinger, H. H. *Organometallics* **2003**, *22*, 1320. (j) Gálvez-Ruiz, J. C.; Nöth, H.; Flores-Parra, A. *Inorg. Chem.* **2003**, *42*, 7569. (k) Liang, L.-C.; Huang, M.-H.; Hung, C.-H. *Inorg. Chem.* **2004**, *43*, 2166. (l) Lewiński, J.; Justyniak, I.; Horeglad, P.; Tratkiewicz, E.; Zachara, J.; Ochal, Z. *Organometallics* **2004**, *23*, 4430.

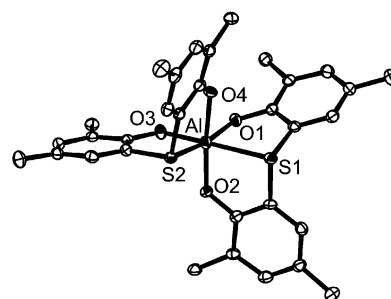


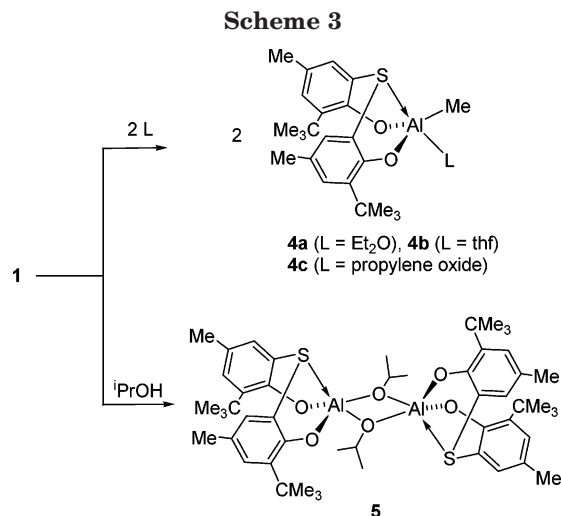
Figure 2. ORTEP diagram of the molecular structure of $[\text{Al}(\text{tbmp})(\text{tbmpH})]$ (**2**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. For all *tert*-butyl groups, only the carbon atoms connected to the phenyl rings are shown. Selected bond lengths (Å) and bond angles (deg): $\text{Al}-\text{O}1 = 1.78(2)$, $\text{Al}-\text{O}2 = 1.748(8)$, $\text{Al}-\text{O}3 = 1.74(2)$, $\text{Al}-\text{O}4 = 2.084(8)$, $\text{Al}-\text{S}1 = 2.56(2)$, $\text{Al}-\text{S}2 = 2.55(2)$.

resonance is shifted to 62 ppm with slight broadening. No decoalescence was observed in the measured temperature range of 0 to -80 °C. We suggest that compound **1** undergoes an exchange process in solution involving five-coordinate aluminum centers in **1'** (Scheme 2). This exchange process can be envisaged as a migration of one of the sulfur donors, changing its coordination site with concomitant migration of one methyl group.

The reaction of AlMe_3 with 2 equiv of tbmpH_2 gave a monomeric compound of composition $[\text{Al}(\text{tbmp})(\text{tbmpH})]$ (**2**) that according to a single-crystal X-ray structure analysis (Figure 2) contains an unsymmetrical six-coordinate entity. The crystal structure solution shows an aluminum atom in two split positions of equal intensity (due to disorder). Each of these positions for the aluminum atom shows short distances to three oxygen atoms (in the range of 1.74(2)–1.79(2) Å) as well as one long distance ($\text{Al}-\text{O}4 = 2.084(8)$ Å, $\text{Al}'-\text{O}2 = 2.059(8)$ Å) to the fourth oxygen atom, which is expected because the oxygen atom of the phenolic unit is protonated. All $\text{Al}-\text{S}$ bond lengths are very similar and in the range of 2.52(2)–2.56(2) Å, somewhat longer than those in **1**. At 25 °C, the ^1H NMR spectrum of **2** in CD_2Cl_2 shows the resonance for the OH group at 7.03 ppm and two sharp singlets for the *tert*-butyl and the *p*-methyl groups, respectively. This simple feature seems to indicate high symmetry for **2**, but variable-temperature NMR spectroscopy shows considerable broadening of all resonances below -40 °C, suggesting that the high symmetry results from the fluxional structure at room temperature. One broad signal at 62 ppm was recorded in the ^{27}Al NMR spectrum (CDCl_3), indicative of the five-coordinate geometry around the aluminum center.¹² It is reasonable to assume that protonation of one of the four oxygen atoms results in the weakening of the coordination to the aluminum atom.

$[\text{Al}(\text{tbmp})(\text{tbmpH})]$ (**2**) could be easily deprotonated with NEt_3 to give the aluminate $[\text{NEt}_3\text{H}][\text{Al}(\text{tbmp})_2]$ (**3**), which contains the nonfluxional, C_2 -symmetric, octahedral anion $[\text{Al}(\text{tbmp})_2]^-$, analogous to $[\text{Ti}(\text{tbmp})_2]^{14a}$ and $[\text{Ti}(\text{mbmp})_2]$.^{14b} When **2** was treated with 1 equiv

(13) (a) Lowe, M. P.; Rettig, S. J.; Orvig, C. *J. Am. Chem. Soc.* **1996**, *118*, 10446. (b) Muñoz-Hernández, M.-A.; Keizer, T. S.; Parkin, S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416.



of AlMe₃ in pentane, the monomethyl compound “[Al(tbmp)Me]” (**1**) formed quantitatively. This stepwise formation of the dinuclear complex **1** corroborates the unsymmetrical structure, which also could be formulated as [AlMe₂][Al(tbmp)₂].

In solutions of dimeric “[Al(tbmp)Me]” (**1**) in coordinating solvents only monomeric species with a five-coordinate aluminum center [Al(tbmp)R(L)] (L = Et₂O, **4a**; THF, **4b**) are observed (Scheme 3). Apparently the Lewis basic solvent molecule L induces a dissociation of the dinuclear species into mononuclear units with concomitant methyl group migration. The ²⁷Al spectrum of **4b** displayed a broad signal at 59 ppm with a shoulder at 98 ppm, indicating a five-coordinate aluminum center. The lability of the Lewis base L might account for the occurrence of the shoulder resonance.^{8g,12} At temperatures below 0 °C, an adduct with the propylene oxide (PO) monomer was isolated as thermally sensitive, feather-like crystals that could be characterized by NMR spectroscopy. It should be noted that the reaction of [Al(tbmp)Me]₂ with PO immediately resulted in ring-opening polymerization.³ Only a few adducts of epoxides that are stable enough to be structurally characterized have been reported before.¹⁵

When the methyl complex **1** was treated with 2-propanol, colorless crystals of the isopropoxide complex [Al(tbmp)(μ-OⁱPr)]₂ (**5**) could be isolated in high yield and completely characterized by NMR spectroscopy and X-ray crystallography (Figure 3). The structure is C_i symmetrical and features two bridging OⁱPr ligands, a very common structural motif in aluminum compounds.^{1e,h} The aluminum centers show a trigonal-bipyramidal coordination geometry, the sulfide group of the tbmp ligand and one μ-OⁱPr group adopting apical positions. The broad signal at 59 ppm in the ²⁷Al NMR spectrum (CDCl₃) further confirmed the dimeric struc-

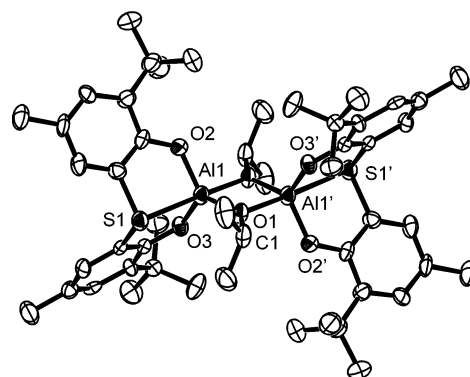


Figure 3. ORTEP diagram of the molecular structure of [Al(tbmp)(μ-OⁱPr)]₂ (**5**). Only one of the two crystallographically independent molecules is shown. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and bond angles (deg): Al1–O1 = 1.794(7), Al1–O1′ = 1.864(7), Al1–O2 = 1.750(8), Al1–O3 = 1.742(8), Al1–S1 = 2.552(5), Al1–Al1′ = 2.828(7); O1–Al1–O1′ = 78.8(4), Al1–O1–Al1′ = 101.2(4).

ture of complex **5** with two five-coordinate aluminum centers in solution.¹² On the basis of the observation that the chemical shifts are invariant to solvent basicity, we assume that the dinuclear structure is retained in solution. Again, the reaction with a protic reagent dramatically changes the unsymmetrical structure of the methyl complex **1**.

Aluminum triethyl behaved analogously to react with the tbmpH ligand, giving the dinuclear complex [Al(tbmp)Et]₂ (**6**). The dissociation reaction of **6** by Lewis bases also gave the mononuclear complexes [Al(tbmp)-Et(L)] (L = Et₂O (**7a**),¹⁶ THF (**7b**)).

In conclusion, we have found an unsymmetrical structure for the monoalkyl complex that functions as a source for the four-coordinate unit “[Al(tbmp)R]” (R = Me, Et). Further studies to elucidate the reactivity in the context of epoxide ring-opening polymerization are underway.

Experimental Section

General Considerations. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Hexane, pentane, diethyl ether, and THF were purified by distillation from sodium/triglyme benzophenone ketyl prior to use. Deuterated solvents and other reagents were carefully dried. 2,2′-Thiobis(6-*tert*-butyl-4-methylphenol) (tbmpH₂) was prepared according to a published procedure.^{6a} Trialkylaluminum compounds in hexane solution from Aldrich were used directly. Propylene oxide was dried over CaH₂ and vacuum condensed prior to use. NMR spectra were recorded on Bruker DRX 400 (¹H, 400 MHz; ¹³C, 100.6 MHz) and Varian Unity 500 (²⁷Al, 130.2 MHz) spectrometers at 25 °C, unless otherwise stated. Chemical shifts for ¹H and ¹³C were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ²⁷Al chemical shifts were referenced to an external 1.1 M solution of Al(NO₃)₃ in D₂O.

[Al(tbmp)Me]₂ (**1**). To a solution of tbmpH₂ (8.92 g, 25 mmol) in hexane (50 mL) was slowly added AlMe₃ (1.90 g, 25 mmol) at room temperature. The mixture was stirred for a

(14) (a) Fokken, S. Doctoral Thesis, Marburg University, 1997. (b) Okuda, J.; Fokken, S.; Kang, H.-C.; Massa, W. *Chem. Ber.* **1995**, *128*, 221.

(15) (a) Groves, J. T.; Han, Y.; Van Engen, D. *J. Chem. Soc., Chem. Commun.* **1990**, 436. (b) Harder, S.; Boersma, J.; Brandsma, L. *Organometallics* **1990**, *9*, 511. (c) Lewinski, J.; Zachara, P.; Horeglad, D.; Glinka, D.; Lipkowski, J.; Justyniak, I. *Inorg. Chem.* **2001**, *40*, 6086. (d) Beckwith, J. D.; Tschinkl, M.; Picot, M.; Tsunoda, R.; Bachmann, F. P.; Gabbai, F. P. *Organometallics* **2001**, *20*, 3169. (e) Dias, H. V. R.; Wang, Z. *Inorg. Chem.* **2000**, *39*, 3724. (f) Darenbourg, D. J.; Holtcamp, M. W.; Khandelwal, B.; Klausmeyer, K. K.; Reibenspies, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 538.

(16) During the revision of this work, complex **7a** was reported: Wasserman, E. P.; Annis, I.; Chopin, L. J., III; Price, P. C.; Petersen, J. L.; Abboud, K. A. *Macromolecules* **2005**, *38*, 322.

further 12 h. Filtration of the precipitate gave 8.70 g (87%) of **1** as a colorless powder. Single crystals were obtained from a hexane solution by slow evaporation of the solvent. ^1H NMR (CDCl_3): δ -1.78 (s, 3 H, AlCH_3), -0.10 (s, 3 H, AlCH_3), 0.84 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.32 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.47 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.56 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 2.13 (s, 3 H, 4- CH_3), 2.15 (s, 3 H, 4- CH_3), 2.25 (s, 3 H, 4- CH_3), 2.30 (s, 3 H, 4- CH_3), 6.90 (1 H, aryl H), 6.96 (1 H, aryl H), 6.98 (1 H, aryl H), 7.13 (1 H, aryl H), 7.29 (3 H, aryl H), 7.35 (1 H, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -11.9 (br, AlCH_3), -5.1 (br, AlCH_3), 20.6 ($2 \times$ 4- CH_3), 20.7 (4- CH_3), 20.8 (4- CH_3), 28.5 (6- $\text{C}(\text{CH}_3)_3$), 29.9 (6- $\text{C}(\text{CH}_3)_3$), 30.5 (6- $\text{C}(\text{CH}_3)_3$), 30.9 (6- $\text{C}(\text{CH}_3)_3$), 34.8 (6- $\text{C}(\text{CH}_3)_3$), 35.1 (6- $\text{C}(\text{CH}_3)_3$), 35.2 (6- $\text{C}(\text{CH}_3)_3$), 35.3 (6- $\text{C}(\text{CH}_3)_3$), 120.6, 122.3, 123.1, 124.0, 125.3, 125.7, 130.1, 130.4, 130.5, 130.7, 132.2, 132.4, 132.7, 133.15, 133.18, 134.4, 138.8, 139.3, 141.3, 141.7, 153.7, 153.8, 157.9, 158.8 (aryl C). ^{27}Al NMR (CDCl_3): δ 52 ($w_{1/2}$ = 4878 Hz). ^{27}Al NMR (CD_2Cl_2 , -80°C): δ 62 ($w_{1/2}$ = 6054 Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{62}\text{Al}_2\text{O}_4\text{S}_2 \cdot 0.5\text{C}_6\text{H}_{14}$: C, 70.05; H, 8.27. Found: C, 70.56; H, 8.19. In an alternative synthesis, AlMe_3 (108 mg, 1.5 mmol) was added to a suspension of $[\text{Al}(\text{tbmp})(\text{tbmpH})]$ (**2**; 1.11 g, 1.5 mmol) in pentane (10 mL). The precipitate was separated by filtration, washed with 5 mL of pentane, and dried under vacuum. The ^1H NMR spectrum of the product was identical with that of the product obtained by the above synthesis; yield 980 mg (82%).

[Al(tbmp)(tbmpH)] (2). To a solution of tbmpH_2 (717 mg, 2.00 mmol) in pentane (20 mL) was slowly added AlMe_3 (0.50 mL, 2.0 M in hexane, 1.0 mmol) at room temperature to give a colorless solution. The reaction mixture was stirred for a further 16 h. After evaporation of the volatiles under vacuum, the residual solid was recrystallized with hexane at -40°C to give colorless prisms; yield 550 mg (74%). ^1H NMR (CDCl_3): δ 1.29 (s, $2 \times$ 18 H, 6- $\text{C}(\text{CH}_3)_3$), 2.21 (s, $2 \times$ 6 H, 4- CH_3), 6.95 (s, 1 H, OH), 7.02 (d, $^4J_{\text{HH}} = 1.6$ Hz, $2 \times$ 2 H, aryl H), 7.24 (d, $^4J_{\text{HH}} = 1.6$ Hz, $2 \times$ 2 H, aryl H). ^1H NMR (C_6D_6): δ 1.44 (s, $2 \times$ 18 H, 6- $\text{C}(\text{CH}_3)_3$), 1.98 (s, $2 \times$ 6 H, 4- CH_3), 7.02 (d, $^4J_{\text{HH}} = 2.0$ Hz, $2 \times$ 2 H, aryl H), 7.12 (s, 1 H, OH), 7.31 (d, $^4J_{\text{HH}} = 2.0$ Hz, $2 \times$ 2 H, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 20.7 (4- CH_3), 29.4 (6- $\text{C}(\text{CH}_3)_3$), 34.8 (6- $\text{C}(\text{CH}_3)_3$), 120.9, 128.0, 130.1, 131.7, 138.0, 155.5 (aryl C). ^{27}Al NMR (CDCl_3): δ 61 ($w_{1/2}$ = 7321 Hz). Anal. Calcd for $\text{C}_{44}\text{H}_{57}\text{AlO}_4\text{S}_2$: C, 71.32; H, 7.75; S 8.65. Found: C, 70.88; H, 7.93; S, 8.87.

[NEt₃H][Al(tbmp)₂] (3). To a suspension of $[\text{Al}(\text{tbmp})(\text{tbmpH})]$ (222 mg, 0.30 mmol) in pentane (20 mL) was added dropwise NEt_3 (40 mg, 0.40 mmol, 0.055 mL). Immediately, a colorless precipitate formed. The mixture was stirred for a further 2 h. The residue was removed by filtration and washed with pentane (10 mL), and the colorless powder was dried under vacuum; yield 170 mg (67%). ^1H NMR (CDCl_3): δ 0.83 (t, $^3J_{\text{HH}} = 7.3$ Hz, 9 H, NCH_2CH_3), 1.17 (s, 18 H, 6- $\text{C}(\text{CH}_3)_3$), 1.39 (s, 18 H, 6- $\text{C}(\text{CH}_3)_3$), 2.12 (s, 6 H, 4- CH_3), 2.22 (s, 6 H, 4- CH_3), 2.52 (q, 6 H, $^3J_{\text{HH}} = 7.3$ Hz, NCH_2CH_3), 4.21 (br s, 1 H, NH), 6.88 (2 H, aryl H), 6.99 (2 H, aryl H), 7.19 (2 H, aryl H), 7.31 (3 H, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3): δ 8.5 (NCH_2CH_3), 20.4 (4- CH_3), 20.5 (4- CH_3), 29.6 (6- $\text{C}(\text{CH}_3)_3$), 29.8 (6- $\text{C}(\text{CH}_3)_3$), 34.7 (6- $\text{C}(\text{CH}_3)_3$), 35.3 (6- $\text{C}(\text{CH}_3)_3$), 47.4 (NCH_2CH_3), 123.3, 123.4, 123.5, 124.1, 128.8, 128.9, 133.3, 138.6, 139.3, 159.5, 159.6 (aryl C). ^{27}Al NMR (CDCl_3): δ 57 ($w_{1/2}$ = 5936 Hz). Anal. Calcd for $\text{C}_{50}\text{H}_{72}\text{AlNO}_4\text{S}_2$: C, 71.30; H, 8.62; N, 1.66; S, 7.61. Found: C, 70.75; H, 8.55; N, 1.79; S, 8.09.

[Al(tbmp)Me(Et₂O)] (4a). A solution of **1** (840 mg, 1.1 mmol) in 6 mL of Et_2O was stored for 16 h at -70°C to afford colorless crystals; yield 780 mg (79%). ^1H NMR (CDCl_3): δ -0.45 (s, 3 H, AlCH_3), 1.36 (s, 18 H, 6- $\text{C}(\text{CH}_3)_3$), 1.39 (t, $^3J_{\text{HH}} = 7$ Hz, 6 H, $\text{CH}_3\text{CH}_2\text{O}$), 2.22 (s, 6 H, 4- CH_3), 4.16 (q, $^3J_{\text{HH}} = 7$ Hz, 4 H, $\text{CH}_3\text{CH}_2\text{O}$), 7.01 (d, $^4J_{\text{HH}} = 2$ Hz, 2 H, aryl H), 7.34 (d, $^4J_{\text{HH}} = 2$ Hz, 2 H, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -14.0 (br, AlCH_3), 13.9 (Et_2O , CH_3CH_2), 20.5 (4- CH_3), 29.4 (6- $\text{C}(\text{CH}_3)_3$), 35.0 (6- $\text{C}(\text{CH}_3)_3$), 65.5 ($\text{CH}_3\text{CH}_2\text{O}$), 122.9, 126.4,

129.7, 132.7, 137.8, 158.5 (aryl C). Anal. Calcd for $\text{C}_{27}\text{H}_{41}\text{AlO}_3\text{S}$: C, 68.61; H, 8.74; S, 6.78. Found: C, 68.53; H, 8.62; S, 6.86.

[Al(tbmp)Me(THF)] (4b). A solution of **1** (600 mg, 0.75 mmol) in THF (8 mL) was stirred for 10 min at room temperature. After evaporation of the solvent under vacuum, the residue was recrystallized from 60 mL of pentane at -70°C to give colorless crystals; yield 580 mg (82%). ^1H NMR (CDCl_3): δ -0.46 (s, 3 H, AlCH_3), 1.41 (s, 18 H, 6- $\text{C}(\text{CH}_3)_3$), 2.17 (br m, 4 H, THF, β - CH_2), 2.26 (s, 6 H, 4- CH_3), 4.42 (br m, 4 H, THF, α - CH_2), 7.05 (d, $^4J_{\text{HH}} = 2$ Hz, 2 H, aryl H), 7.39 (d, $^4J_{\text{HH}} = 2$ Hz, 2 H, aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -8.6 (br, AlCH_3), 20.5 (4- CH_3), 25.4 (THF, β - CH_2), 29.4 (6- $\text{C}(\text{CH}_3)_3$), 35.0 (6- $\text{C}(\text{CH}_3)_3$), 71.2 (THF, α - CH_3), 122.9, 126.2, 129.6, 132.6, 137.6, 158.6 (aryl C). ^{27}Al NMR (CDCl_3): δ 59 ($w_{1/2}$ = ca. 3749 Hz), 98 (shoulder). Anal. Calcd for $\text{C}_{27}\text{H}_{39}\text{AlO}_3\text{S}$: C, 68.90; H, 8.35; S, 6.81. Found: C, 68.48; H, 8.21; S, 7.30.

[Al(tbmp)Me(propylene oxide)] (4c). To a solution of **1** (200 mg, 0.25 mmol) in pentane (50 mL) was slowly added propylene oxide (0.35 mL, 290 mg, 5 mmol) with stirring at -20°C . Stirring was continued for 1.5 h at -20°C . The solution was kept at -70°C overnight; a colorless precipitate formed. This was separated and dried under vacuum; yield 135 mg (59%). Recrystallization from pentane gave thin needles. ^1H NMR (CDCl_3): δ -0.54 (s, 3 H, AlCH_3), 1.36 (s, 18 H, 6- $\text{C}(\text{CH}_3)_3$), 1.66 (d, $^3J_{\text{HH}} = 5.5$ Hz, 3 H, $\text{CH}_3\text{C}_2\text{H}_5\text{O}$), 2.22 (s, 6 H, 4- CH_3), 3.21 (t, $^3J_{\text{HH}} = 3.5$ Hz, 1 H, $\text{CH}_3\text{CH}_2\text{O}$), 3.75 (t, $^3J_{\text{HH}} = 4.1$ Hz, 1 H, $\text{CH}_3\text{CH}_2\text{O}$), 4.02 (m, $^3J_{\text{HH}} = 5.1$ Hz, 1 H, $\text{CH}_3\text{CH}_2\text{O}$), 7.00 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2 H, 5-H), 7.33 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2 H, 3-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , -60°C): δ -11.2 (AlCH_3), 15.9 ($\text{CH}_3\text{CH}_2\text{O}$), 29.4 (4- CH_3), 27.8 (6- $\text{C}(\text{CH}_3)_3$), 33.9 (6- $\text{C}(\text{CH}_3)_3$), 53.4 ($\text{CH}_3\text{CH}_2\text{O}$), 57.5 ($\text{CH}_3\text{CH}_2\text{O}$), 121.5, 125.6, 128.8, 130.9, 136.6, 156.9 (aryl C). Anal. Calcd for $\text{C}_{26}\text{H}_{37}\text{AlO}_3\text{S}$: C, 68.39; H, 8.17; S, 7.02. Found: C, 67.51; H, 7.78; S, 7.89.

[Al(tbmp)(μ -OⁱPr)]₂ (5). To a suspension of **1** (1.20 g, 1.5 mmol) in hexane (40 mL) was slowly added 2-propanol (0.23 mL, 180 mg, 3.0 mmol) at room temperature. From the initially clear solution, a colorless precipitate formed slowly. To complete the precipitation, stirring was continued for a further 16 h at room temperature. The colorless precipitate of $[\text{Al}(\text{tbmp})(\mu\text{-O}^i\text{Pr})]_2$ was separated by filtration, washed with hexane (10 mL), and dried under vacuum; yield 950 mg (72%). Leaving the mother liquor for 1 week at -30°C gave colorless crystals. ^1H NMR (C_6D_6): δ 1.48 (s, 36 H, 6- $\text{C}(\text{CH}_3)_3$), 1.63 (d, $^3J_{\text{HH}} = 6.4$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 2.07 (s, 12 H, 4- CH_3), 4.87 (septet, $^3J_{\text{HH}} = 6.4$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.13 (d, $^4J_{\text{HH}} = 1.4$ Hz, 4 H, 5-H), 7.48 (d, $^4J_{\text{HH}} = 1.4$ Hz, 4 H, 3-H). ^1H NMR (THF- d_6): δ 1.35 (s, 36 H, 6- $\text{C}(\text{CH}_3)_3$), 1.58 (d, $^3J_{\text{HH}} = 6.5$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$), 2.22 (s, 12 H, 4- CH_3), 4.75 (septet, $^3J_{\text{HH}} = 6.5$ Hz, $\text{CH}(\text{CH}_3)_2$), 7.07 (d, $^4J_{\text{HH}} = 1.6$ Hz, 4 H, 5-H), 7.43 (d, $^4J_{\text{HH}} = 1.6$ Hz, 4 H, 3-H). $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_6): δ 20.9 (4- CH_3), 26.1 ($\text{CH}(\text{CH}_3)_2$), 30.0 (6- $\text{C}(\text{CH}_3)_3$), 36.1 (6- $\text{C}(\text{CH}_3)_3$), 69.9 ($\text{CH}(\text{CH}_3)_2$), 122.1, 128.5, 131.5, 132.7, 139.5, 158.4 (aryl C). ^{27}Al NMR (CDCl_3): δ 59 ($w_{1/2}$ = 5514 Hz). Anal. Calcd for $\text{C}_{25}\text{H}_{35}\text{AlO}_3\text{S}$: C, 67.84; H, 7.97; S, 7.24. Found: C, 67.89; H, 8.08; S, 7.07.

[Al(tbmp)Et]₂ (6). To a solution of tbmpH_2 (1.79 g, 5.0 mmol) in pentane (70 mL) was added dropwise AlEt_3 (0.57 g, 5.0 mmol) at 0°C . After several minutes, a colorless precipitate formed. The mixture was stirred for a further 6 h at room temperature. The precipitate was separated by filtration, washed twice with pentane (20 mL), and dried under vacuum; yield 1.6 g (78%). ^1H NMR (CDCl_3): δ -1.11 (m, $^3J_{\text{HH}} = 8.0$ Hz, 4 H, AlCH_2CH_3), 0.14 (t, $^3J_{\text{HH}} = 8.0$ Hz, 6 H, AlCH_2CH_3), 0.66 (s, 2 H, AlCH_2CH_3), 0.78 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.01 (t, $^3J_{\text{HH}} = 8.0$ Hz, 3 H, AlCH_2CH_3), 1.30 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.43 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 1.55 (s, 9 H, 6- $\text{C}(\text{CH}_3)_3$), 2.08 (s, 3 H, 4- CH_3), 2.10 (s, 3 H, 4- CH_3), 2.21 (s, 3 H, 4- CH_3), 2.28 (s, 3 H, 4- CH_3), 6.85-7.32 (aryl H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ -1.3 (br, AlCH_2CH_3), 4.7 (br, AlCH_2CH_3), 8.4 (AlCH_2CH_3), 9.0 (AlCH_2CH_3),

20.6 (2 × 4-CH₃), 20.7 (4-CH₃), 20.8 (4-CH₃), 28.4 (6-C(CH₃)₃), 29.9 (6-C(CH₃)₃), 30.4 (6-C(CH₃)₃), 30.8 (6-C(CH₃)₃), 34.8 (6-C(CH₃)₃), 35.1 (6-C(CH₃)₃), 35.1 (6-C(CH₃)₃), 35.3 (6-C(CH₃)₃), 120.6, 122.4, 123.4, 124.2, 125.3, 125.7, 130.1, 130.3, 130.4, 130.7, 132.3, 132.4, 132.7, 133.1, 133.3, 134.6, 138.7, 139.4, 141.4, 141.7 (phenyl C-2 to C-6), 153.7, 153.8, 157.9, 158.8 (phenyl *ipso*-C). ²⁷Al NMR (CDCl₃): δ 52 (*w*_{1/2} = 5155 Hz). Anal. Calcd for C₄₈H₆₆Al₂O₄S₂: C, 69.87; H, 8.06; S, 7.77. Found: C, 70.01; H, 8.01; S, 7.83.

[Al(tbmp)Et(Et₂O)] (7a). [Al(tbmp)Et]₂ (0.619 g, 0.75 mmol) was dissolved in Et₂O (35 mL) and the solution stirred at room temperature for 2 h. After the volume of the solution was reduced to 10 mL under reduced pressure, the solution was cooled to -20 °C for 12 h. During this time, colorless crystals of the product formed. Additional product was obtained by further concentration of the solution under vacuum; yield 550 mg (75%). ¹H NMR (CDCl₃): δ 0.16 (q, ³J_{HH} = 8.0 Hz, 2 H, AlCH₂CH₃), 1.06 (t, ³J_{HH} = 8.0 Hz, 3 H, AlCH₂CH₃), 1.36 (s, 18 H, 6-C(CH₃)₃), 1.41 (t, ³J_{HH} = 7.0 Hz, 6 H, (CH₃-CH₂)₂O), 2.22 (s, 6 H, 4-CH₃), 4.25 (q, ³J_{HH} = 7.0 Hz, 4 H, (CH₃CH₂)₂O), 7.01 (d, ⁴J_{HH} = 2.0 Hz, 2 H, 5-CH), 7.36 (d, ⁴J_{HH} = 2.0 Hz, 2 H, 3-CH). ¹³C{¹H} NMR (CDCl₃): δ 2.7 (AlCH₂-CH₃), 9.3 (AlCH₂CH₃), 13.9 ((CH₃CH₂)₂O), 20.5 (4-CH₃), 29.4 (6-C(CH₃)₃), 34.9 (6-C(CH₃)₃), 65.5 ((CH₃CH₂)₂O), 122.7, 126.4, 129.7, 132.6, 137.8, 158.7 (aryl C). Anal. Calcd for C₂₈H₄₃-AlO₃S: C, 69.10; H, 8.90; S, 6.59. Found: C, 69.29; H, 9.03; S, 6.56.

[Al(tbmp)Et(THF)] (7b). [Al(tbmp)Et]₂ (0.413 g, 0.5 mmol) was dissolved in THF (4 mL) and the solution stirred at room temperature for 30 min. The solvent was removed under vacuum, leaving the product as a colorless powder that was washed with pentane; yield 225 mg (46%). ¹H NMR (CDCl₃): δ 0.16 (q, ³J_{HH} = 8.3 Hz, 2 H, AlCH₂CH₃), 1.08 (t, ³J_{HH} = 8.2 Hz, 3 H, AlCH₂CH₃), 1.40 (s, 18 H, 6-C(CH₃)₃), 2.18 (m, 4 H, THF, β-CH₂), 2.25 (s, 6 H, 4-CH₃), 4.45 (m, 4 H, THF, α-CH₂), 7.04 (d, ⁴J_{HH} = 1.6 Hz, 2 H, 5-H), 7.39 (d, ⁴J_{HH} = 1.6 Hz, 2 H, 3-H). ¹³C{¹H} NMR (CDCl₃): δ: 1.7 (AlCH₂CH₃), 9.4 (AlCH₂CH₃), 20.6 (4-CH₃), 25.4 (THF, β-CH₂), 29.3 (6-C(CH₃)₃), 35.0 (6-C(CH₃)₃), 71.4 (THF, α-CH₃), 122.7, 126.2, 129.6, 132.6, 137.6, 158.8 (aryl C). ²⁷Al NMR (CDCl₃): δ 60 (*w*_{1/2} = ca. 3593 Hz), 99 (shoulder). Anal. Calcd for C₂₈H₄₁AlO₃S: C, 69.39; H, 8.53; S, 6.62. Found: C, 68.94; H, 8.39; S, 6.85.

X-Ray Crystal Structure Analysis of [Al(tbmp)Me]₂ (1), [Al(tbmp)(tbmpH)] (2), and [Al(tbmp)(μ-OⁱPr)]₂ (5). Single crystals suitable for an X-ray crystal structure analysis were obtained by cooling concentrated hexane solutions to -30 °C for **1** and **5** as well as by slow evaporation of a saturated hexane solution at room temperature for **2**. The data sets for **1** and **5** were obtained with an Enraf-Nonius CAD4 diffractometer using ω scans. Crystal parameters and results of the structure refinements are given in Table 1. The data reductions were performed using the program system WinGX.¹⁷ The data set of **2** was obtained with a Bruker AXS diffractometer at 120 K using ω scans. The data reduction was performed using the program system SMART.¹⁸ All structures were solved by direct methods and difference Fourier syntheses using the program system SHELXS-86.¹⁹ The crystallographic unit cell of **5** contains two independent molecules, which are

Table 1. Crystallographic Data for **1**, **2**, and **5**

	1	2	5
formula	C ₄₆ H ₆₂ Al ₂ O ₄ -S ₂ ·0.5C ₆ H ₁₄	C ₄₄ H ₅₇ AlO ₄ S ₂	C ₅₀ H ₇₀ Al ₂ O ₆ -S ₂ ·C ₆ H ₁₄
<i>M_r</i>	840.12	741.00	971.31
temp/K	296(2)	120(2)	296(2)
cryst size/mm	0.40 × 0.30 × 0.25	0.48 × 0.31 × 0.23	0.30 × 0.30 × 0.10
cryst syst	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
<i>a</i> /Å	13.2800(7)	9.559(2)	10.6666(9)
<i>b</i> /Å	19.642(1)	13.862(3)	13.628(1)
<i>c</i> /Å	21.136(1)	16.054(3)	20.989(2)
α/deg	90	78.795(4)	82.473(7)
β/deg	105.115(4)	79.940(4)	78.028(7)
γ/deg	90	85.493(4)	78.106(6)
<i>V</i> /Å ³	5322.5(5)	2052.7(7)	2908.2(4)
<i>Z</i>	4	2	2
<i>D_c</i> /g cm ⁻³	1.048	1.199	1.109
μ/mm ⁻¹	0.170	0.191	0.166
<i>F</i> (000)	1812	796	1052
θ range/deg	3–24	2–28	3–20
data collected (<i>hkl</i>)	-13 to +15, -20 to +22, -24 to +23	±12, ±18, ±21	0–10, -12 to +13, -19 to +20
no. of rflns collected	23 708	28 433	5777
no. of indep rflns	8298	10 150	5390
<i>R</i> _{int}	0.2001	0.0441	0.0897
final <i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0777, 0.2039	0.0610, 0.1283	0.0779, 0.1179
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.2672, 0.2920	0.0794, 0.1332	0.3016, 0.1665
goodness of fit on <i>F</i> ²	1.090	1.161	0.939
Δρ _{max,min} /e Å ⁻³	0.571, -0.309	0.364, -0.271	0.233, -0.200

located around centers of inversion. The refinements based on *F*² were carried out using the program SHELXL-97.²⁰ Anisotropic thermal parameters were refined for the non-hydrogen atoms (except for the disordered groups). Hydrogen atoms were included into calculated positions. For the crystal structure of compound **2**, two split positions of the disordered hydrogen atom were localized near the atoms O2 and O4 in a Fourier difference map. These hydrogen atoms were included in the refinement with a multiplicity of 0.5, and their positions were not refined. In addition, the aluminum atom was refined with two split positions of equal occupancies. Both crystals **1** and **5** contain molecules of hexane in disordered positions. Due to the severe disorder, the refinement was difficult. The carbon atoms were fixed in their positions; only their isotropic thermal parameters were refined.

Acknowledgment. We thank Bayer AG, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie for financial support. We also thank Prof. U. Englert for helpful discussions.

Supporting Information Available: Tables of all crystal data and refinement parameters, atomic parameters, including hydrogen atoms, thermal parameters, and bond lengths and angles for **1**, **2**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM049067B

(17) Farrugia, L. J.; *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(18) ASTRO, SAINT, and SADABS: Data Collection and Processing Software for the SMART System; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.

(19) Sheldrick, G. M.; SHELXS-86, A Program for Crystal Structure Solution; University of Göttingen, Göttingen, Germany, 1986.

(20) Sheldrick, G. M.; SHELXL-97, A Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.