1246 *Organometallics* **2010,** *29,* 1246–1260
DOI: 10.1021/om901070g

ORGANOMETALLICS
Article

Sulfonamide-Supported Aluminum Catalysts for the Ring-Opening Polymerization of *rac*-Lactide

Andrew D. Schwarz, Zengyong Chu, and Philip Mountford*

Chemistry Research Laboratory, University of Oxford, Mansfield Road, Oxford OX1 3TA, U.K.

Received December 14, 2009

The synthesis, structures, and ring-opening polymerization (ROP) capability of a wide range of sulfonamide-supported aluminum alkyl and alkoxide complexes are reported. The synthesis of the new protio-ligands $PhCH_2N(CH_2CH_2NHSO_2R)_2$ (R = Tol (**15**, $H_2N_2^{Ts}N^{Ph}$) or Me (**16**, $H_2N_2^{Ms}N^{Ph}$)) is described. These and the previously reported 1,2-$C_6H_{10}(NHSO_2R)_2$ (R = Tol (**11**, $H_2CyN_2^{Ts}$) or Mes (**12**, $H_2CyN_2^{SO_2Mes}$)) and $RCH_2N(CH_2CH_2NHSO_2Tol)_2$ (R = $MeOCH_2$ (**13**, $H_2N_2^{Ts}N^{OMe}$) or 2-NC_5H_4 (**14**, $H_2N_2^{Ts}N^{py}$)) reacted with $AlEt_3$ to form $Al(CyN_2^{Ts})Et(THF)$ (**17**), $Al(CyN_2^{SO_2Mes})Et(THF)$ (**18**), and $Al(N_2^{Ts}N^{R})Et$ (R = Ph (**19**), OMe (**20**), or py (**21**)), respectively. Subsequent reaction of these ethyl complexes with $R'OH$ (R' = ^{i}Pr or Bn) resulted in protonolysis of the sulfonamide supporting ligands to yield a mixture of products including $Al(OR')_3$. In contrast, reaction of $Al(OR')Et_2$ (R' = ^{i}Pr, Bn, $CH_2CH_2NH_2$, or $CH_2CH_2NMe_2$) with various protio-ligands formed the sulfonamide-supported alkoxides $Al(N_2^{Ts}N^{py})(OR')$ (R' = ^{i}Pr (**22**) or Bn (**23**)), $Al(N_2^{Ms}N^{Ph})(OR')$ (R' = ^{i}Pr (**26**) or Bn (**27**)), $Al(N_2^{Ts}N^{R})(OCH_2CH_2NH_2)$ (R = Ph (**29**), OMe (**30**), or py (**31**)), $Al(CyN_2^{Ts})(OCH_2CH_2NMe_2)$ (**32**), and $Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**33**). Unexpectedly, reaction of $Al(O^{i}Pr)Et_2$ with $H_2N_2^{Ts}N^{OMe}$ led to O-demethylation of the sulfonamide ligand. Reaction of $AlMe_2Cl$ with $H_2N_2^{Ts}N^{Ph}$ gave $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (**28**). X-ray diffraction studies revealed four- or five-coordinate C_s-symmetric structures for **17**−**21**, a five-coordinate C_2-symmetric sulfonamide-bridged dimer for **28**, and a five-coordinate C_s-symmetric monomer for **30** stabilized by intramolecular hydrogen bonding between the sulfonyl oxygens and the amine protons. Compounds **19**, 21, **22**−**27**, and **29**−**33** are all catalysts for the ROP of *rac*-lactide, with the alkoxide compounds 22−**27** and **32** giving well-defined molecular weights and molecular weight distributions. These compounds were also active in the melt at 130 °C, giving atactic poly(*rac*-lactide) with moderate to narrow PDIs and extremely good control of M_n and high activity in the case of **23**.

Introduction

Polyesters derived from lactic acid are currently the focus of intense research due to the biocompatibility and biodegradability of the resulting polymers. Derived from 100% renewable resources including corn and sugar beet, these polymers can act as replacements for oil-based materials.[1−7] In industry, these materials are synthesized by the metal-catalyzed ring-opening polymerization (ROP) of the cyclic ester lactide (LA).[3] Metal-based catalysts for the ROP of cyclic esters are generally derived from Lewis acidic metals, feature one or more alkoxide functional (initiating) groups, and are supported by a polydentate ancillary ligand (set) that controls the catalyst nuclearity and coordination−insertion chain growth mechanism. It is an area of research that has been extensively reviewed recently.[8−11] Catalyst systems can be based on many metals such as magnesium,[12−16] zinc,[12,14,16−20]

---

*Corresponding author. E-mail: philip.mountford@chem.ox.ac.uk.

(1) Emo, C.; Roberto, S. *Adv. Mater.* **1996**, *8*, 305–313.

(2) Uhrich, K. E.; Cannizzaro, S. M.; Langer, R. S.; Shakesheff, K. M. *Chem. Rev.* **1999**, *99*, 3181–3198.

(3) Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841–1846.

(4) Yoshito, I.; Hideto, T. *Macromol. Rapid Commun.* **2000**, *21*, 117–132.

(5) Stefan, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1078–1085.

(6) Williams, C. K.; Hillmyer, M. A. *Polym. Rev.* **2008**, *48*, 1–10.

(7) Place, E. S.; George, J. H.; Williams, C. K.; Stevens, M. M. *Chem. Soc. Rev.* **2009**, *38*, 1139–1151.

(8) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147–6176.

(9) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215–2224.

(10) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11–63.

(11) Kamber, N. E.; Jeong, W.; Waymouth, R. M.; Pratt, R. C.; Lohmeijer, B. G. G.; Hedrick, J. L. *Chem. Rev.* **2007**, *107*, 5813–5840.

(12) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238.

(13) Chisholm, M. H.; Eilerts, N. W. *Chem. Commun.* **1996**, 853–854.

(14) Chisholm, M. H.; Huffman, J. C.; Phomphrai, K. *J. Chem. Soc., Dalton Trans.* **2001**, 222–224.

(15) Wheaton, C. A.; Hayes, P. G.; Ireland, B. J. *Dalton Trans.* **2009**, 4832–4846.

(16) Poirier, V.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Dalton Trans.* **2009**, 9820–9827.

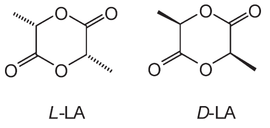
(17) Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583–11584.

(18) Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845–11854.

(19) Wheaton, C. A.; Ireland, B. J.; Hayes, P. G. *Organometallics* **2009**, *28*, 1282–1285.

(20) Chisholm, M. H.; Lin, C.-C.; Gallucci, J. C.; Ko, B.-T. *Dalton Trans.* **2003**, 406–412.

calcium,^{15,16,21,22} aluminum,$^{20,23-26}$ yttrium,$^{27-29}$ the lanthanides,$^{30-33}$ tin,^{34} the group 4 elements,$^{20,35-42}$ germanium,^{43} indium,^{44} and iron.^{45,46}



rac-lactide (*rac*-LA)

Aluminum catalysts have been extensively exploited for the ROP of *rac*-LA with many examples of predictable molecular weights, narrow polydispersities (PDIs), and either heterotactic or isotactic enrichment being achieved. Notable examples of aluminum-based catalysts are the salen$^{47-60}$ and salan^{61} complexes with which highly isotactic, syndiotactic, or tapered isotactic block copolymers can be formed, depending on the stereoisomer of the LA and salen ligands employed (e.g., **1**−**5**, Figure 1). Complexes of polydentate phenoxy-amine ligands (e.g., **6**, Figure 1) have also been investigated for the ROP of both *rac*-LA and ε-caprolactone.$^{62-66}$ Interesting, and at times contradictory, steric and electronic effects of ligand variation upon catalysis have been observed for these systems. A prime example is the system studied by Hillmyer and Tolman^{64} (**6**) in which substituting the *tert*-butyl substituent in the 5-position of the phenolate ring for bromine significantly decreases activity. This is in stark contrast to the corresponding salen

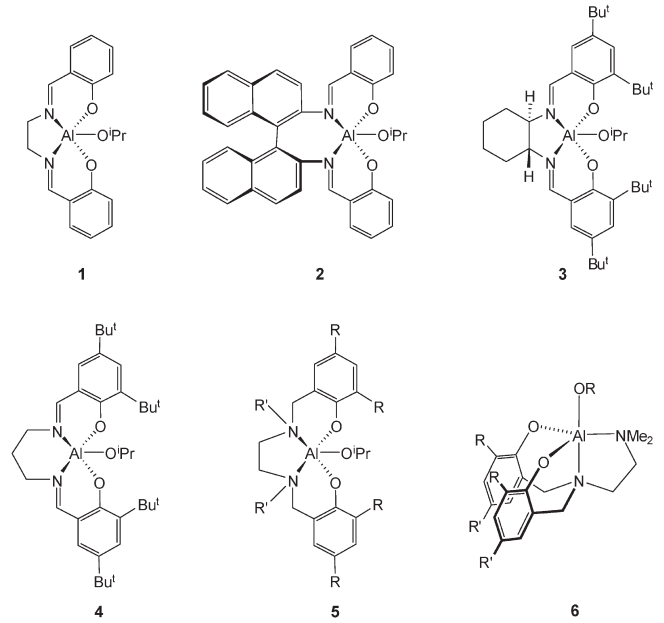


Figure 1. Examples of phenolate-supported aluminum catalysts for the ROP of cyclic esters.$^{47-61}$

---

(21) Zhong, Z.; Dijkstra, P. J.; Birg, C.; Westerhausen, M.; Feijen, J. *Macromolecules* **2001**, *34*, 3863–3868.

(22) Antelmann, B.; Chisholm, M. H.; Iyer, S. S.; Huffman, J. C.; Navarro-Llobet, D.; Pagel, M.; Simonsick, W. J.; Zhong, W. *Macromolecules* **2001**, *34*, 3159–3175.

(23) Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *24*, 977–981.

(24) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114–2122.

(25) Aida, T.; Inoue, S. *Acc. Chem. Res.* **1996**, *29*, 39–48.

(26) Paul, A.; Cameron; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616–618.

(27) McLain, S. J.; Ford, T. M.; Drysdale, N. E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Sci.*) **1992**, *33*, 463.

(28) Chamberlain, B. M.; Sun, Y.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G., Jr.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400–2402.

(29) Cai, C.-X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J.-F. *Chem. Commun.* **2004**, 330–331.

(30) Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923–927.

(31) Dyer, H. E.; Huijser, S.; Schwarz, A. D.; Wang, C.; Duchateau, R.; Mountford, P. *Dalton Trans.* **2008**, 32–35.

(32) Bonnet, F.; Cowley, A. R.; Mountford, P. *Inorg. Chem.* **2005**, *44*, 9046–9055.

(33) Ma, H.; Okuda, J. *Macromolecules* **2005**, *38*, 2665–2673.

(34) Kricheldorf, H. R.; Kreiser-Saunders, I.; Boettcher, C. *Polymer* **1995**, *36*, 1253–1259.

(35) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286–293.

(36) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437–1447.

(37) Thomas, D.; Arndt, P.; Peulecke, N.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Eur. J. Inorg. Chem.* **1998**, 1351−1357.

(38) Dobrzynski, P.; Li, S.; Kasperczyk, J.; Bero, M.; Gasc, F.; Vert, M. *Biomacromolecules* **2005**, *6*, 483–488.

(39) Mogstad, A.-L.; Waymouth, R. M. *Macromolecules* **1994**, *27*, 2313–2315.

(40) Miola Delaite, C.; Hamaide, T.; Spitz, R. *Macromol. Chem. Phys.* **1999**, *200*, 1771–1778.

(41) Hsieh, K. C.; Lee, W. Y.; Hsueh, L. F.; Lee, H. M.; Huang, J. H. *Eur. J. Inorg. Chem.* **2006**, 2306–2312.

(42) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, 6804–6806.

(43) Chmura, A. J.; Chuck, C. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Bull, S. D.; Mahon, M. F. *Angew. Chem., Int. Ed.* **2007**, *46*, 2280–2283.

(44) Douglas, A. F.; Patrick, B. O.; Mehrkhodavandi, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 2290–2293.

(45) O'Keefe, B. J.; Monnier, S. M.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2001**, *123*, 339–340.

(46) O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384–4393.

(47) Tang, Z.; Chen, X.; Pang, X.; Yang, Y.; Zhang, X.; Jing, X. *Biomacromolecules* **2004**, *5*, 965–970.

(48) Zhaohui, T.; Xuesi, C.; Yongkun, Y.; Xuan, P.; Jingru, S.; Xuefei, Z.; Xiabin, J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5974–5982.

(49) Wisniewski, M.; Borgne, A. L.; Spassky, N. *Macromol. Chem. Phys.* **1997**, *198*, 1227–1238.

(50) Spassky, N.; Wisniewski, M.; Pluta, C.; LeBorgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627.

(51) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316.

(52) Ovitt, T. M.; Coates, G. W. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 4686–4692.

(53) Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552.

(54) Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 4510.

(55) Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *J. Am. Chem. Soc.* **2003**, *125*, 11291.

(56) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938.

(57) Chisholm, M. H.; Gallucci, J. C.; Quisenberry, K. T.; Zhou, Z. *Inorg. Chem.* **2008**, *47*, 2613–2624.

(58) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.−Eur. J.* **2007**, *13*, 4433.

(59) Du, H. Z.; Pang, X.; Yu, H. Y.; Zhuang, X. L.; Chen, X. S.; Cui, D. M.; Wang, X. H.; Jing, X. B. *Macromolecules* **2007**, *40*, 1904.

(60) Jing, Y.; Qiaobo, L.; Yang, L.; Lin, J.; Qiang, F.; Amin, C. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 2045–2058.

(61) Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688–2689.

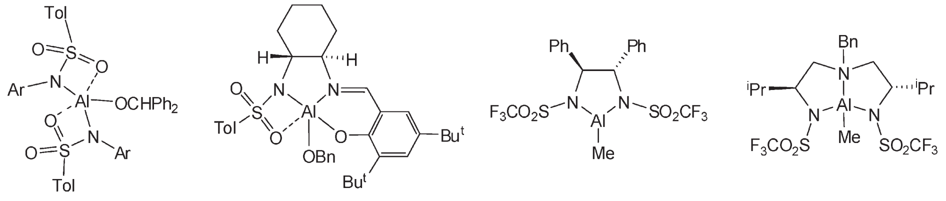
(62) Johnson, A. L.; Davidson, M. G.; Perez, Y.; Jones, M. D.; Merle, N.; Raithby, P. R.; Richards, S. P. *Dalton Trans.* **2009**, 5551–5558.

(63) Tang, Z.; Gibson, V. C. *Eur. Polym. J.* **2007**, *43*, 150–155.

(64) Alcazar-Roman, L. M.; O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *Dalton Trans.* **2003**, 3082–3087.

(65) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Dalton Trans.* **2003**, 3799–3803.

(66) Chen, C.-T.; Huang, C.-A.; Huang, B.-H. *Macromolecules* **2004**, *37*, 7968–7973.



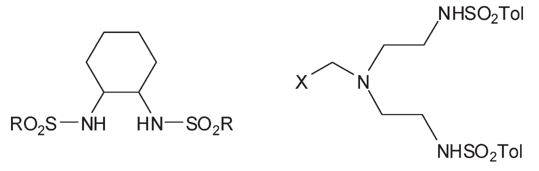
7 **8** **9** **10**

Figure 2. Previously reported examples of aluminum sulfonamide complexes.[74−77]

ligands, for which Gibson showed halide substituents on the phenolate ring *enhanced* activity.[26] Therefore, work aimed at clarifying catalyst structure−activity relationships though systematic ligand variation and evaluation of catalytic performance is of high value.

Very recently, we described the use of tetradentate sulfonamides (containing $-N(R)SO_2R'$ donors) as supporting ligands for group 4 ROP catalysts.[67] These catalysts effected the highly controlled ROP of *rac*-LA and ε-caprolactone, giving polymers with narrow PDIs and predictable M_n values in a living fashion. They gave comparable performances to the well-established bis(phenolate) systems extensively studied by Kol and Davidson.[68−72] In particular, zirconium catalysts of the tetradentate ligand $N_2^{Ts}N^{OMe}$ (**13**; see Figure 3) allowed excellent control of the polymerization process in toluene solution at elevated temperature, albeit with no stereochemical bias, yielding atactic polymer.[67] In these group 4 catalysts, the electron-withdrawing SO_2R' moieties reduce the usual basicity of anionic amide donors "NR_2" and therefore allowed them to act as phenolate mimics. Furthermore, although $N(R)SO_2R'$-based ligands lack the steric control afforded by bulky ring-substituted phenolates OAr (e.g., **3−6**, Figure 1), the well-established ability of sulfonamide ligands to adopt $\kappa^2(N,O)$ coordination modes confers additional stability on otherwise unsaturated metal centers.[73]

To date, there have been only two examples of sulfonamide-supported aluminum ROP catalysts, namely, **7** and **8** in Figure 2.[74,75] Compound **7** gave poor control of the polymerization process with a much lower than expected M_n and a moderately broad PDI under melt conditions after 10 h at 130 °C. In contrast, **8** showed excellent control in the polymerization of L-LA, yielding predominantly isotactic polymers with narrow PDIs and close agreement between expected M_n values and those measured by GPC.[75] In general a number of aluminum sulfonamide complexes have been reported (e.g., **9** and **10**) and employed for transformations such as enantioselective catalytic Diels−Alder reactions,[76] asymmetric aldehyde cycloaddition reactions,[77,78] the Meerwein−Ponndorf−Verley reduction of carbonyl substrates,[79] the enantioselective [2+2] cycloaddition of trimethylsilylketene to aldehydes,[80] and the cyclopropanation of allylic alcohols.[81]



R = Tol (**11**) or Mes (**12**) X =CH_2OMe (**13**) or 2-NC_5H_4 (**14**)

Figure 3. Previously reported protio-ligands employed in this study.

Our success with sulfonamide-supported group 4 ROP catalysts, and the promising results recently reported for **8**, prompted us to develop and evaluate a series of aluminum-based ROP catalysts using this type of ligand. Alongside the tetradentate ligands that we employed previously, we have also used homologous bidentate and tridentate systems, since the radius of aluminum is somewhat smaller than those of the group 4 metals. In this contribution we report the synthesis, structures, and ring-opening polymerization (ROP) capability of a wide range of sulfonamide-supported aluminum alkyl and alkoxide complexes.

Results and Discussion

Synthesis. The previously reported bidentate and tetradentate protio-ligands (Figure 3) $H_2CyN_2^{Ts}$ (**11**),[82] $H_2CyN_2^{SO_2Mes}$ (**12**),[83] $H_2N_2^{Ts}N^{OMe}$ (**13**),[84] and $H_2N_2^{Ts}N^{py}$ (**14**)[85] were synthesized according to literature methods.

To further explore the effects of metal coordination number and sulfonamide group R-substituent on the

---

(67) Schwarz, A. D.; Thompson, A. L.; Mountford, P. *Inorg. Chem.* **2009**, *48*, 10442–10454.

(68) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F.; Johnson, A. F.; Khunkamchoo, P.; Roberts, S. L.; Wong, S. S. F. *Macromolecules* **2006**, *39*, 7250–7257.

(69) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2006**, 887–889.

(70) Chmura, A. J.; Cousins, D. M.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2008**, 1437–1443.

(71) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293–1295.

(72) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783–4790.

(73) Massimiliano, F.; Fredrik, L.; Myriam Mba, B.; Patrick, R.; Marco, C.; Lutz, H. G.; Giulia, L.; Christina, M. *Eur. J. Inorg. Chem.* **2006**, 1032–1040.

(74) Zhao, J.; Song, H.; Cui, C. *Organometallics* **2007**, *26*, 1947–1954.

(75) Wu, J.; Pan, X.; Tang, N.; Lin, C.-C. *Eur. Polym. J.* **2007**, *43*, 5040–5046.

(76) Corey, E. J.; Sarshar, S.; Lee, D.-H. *J. Am. Chem. Soc.* **1994**, *116*, 12089–12090.

(77) Nelson, S. G.; Kim, B.-K.; Peelen, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 9318–9319.

(78) Nelson, S. G.; Peelen, T. J.; Wan, Z. *J. Am. Chem. Soc.* **1999**, *121*, 9742–9743.

(79) Takashi, O.; Hayato, I.; Keiji, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3610–3612.

(80) Dymock, B. W.; Kocienski, P. J.; Pons, J. M. *Chem. Commun.* **1996**, 1053–1054.

(81) Imai, N.; Takahashi, H.; Kobayashi, S. *Chem, Lett.* **1994**, 177–180.

(82) Kitagawa, O.; Yotsumoto, K.; Kohriyama, M.; Dobashi, Y.; Taguchi, T. *Org. Lett.* **2004**, *6*, 3605–3607.

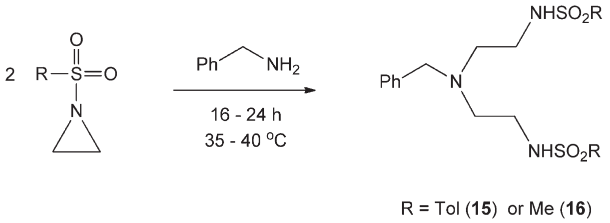
(83) Takahashi, H.; Kawakita, T.; Ohno, M.; Yoshioka, M.; Kobayashi, S. *Tetrahedron* **1992**, *48*, 5691–5700.

(84) Bailey, N. A.; Fenton, D. E.; Hellier, P. C.; Hempstead, P. D.; Casellatob, U.; Vigatob, P. A. *Dalton Trans.* **1992**, 2809–2816.

(85) Skinner, M. E. G.; Li, Y.; Mountford, P. *Inorg. Chem.* **2002**, *41*, 1110–1119.

structures and ROP properties of the new catalysts, the new tridentate protio-ligands $\mathrm{PhCH_2N(CH_2CH_2NHSO_2R)_2}$ (R = Tol (**15**, $H_2N_2^{Ts}N^{Ph}$) or Me (**16**, $H_2N_2^{Ms}N^{Ph}$)) were synthesized. Using a similar synthetic route to that for **13** and **14**, reaction of benzyl amine with the appropriate *N*-sulfonyl aziridine gave good yields of **15** and **16** (eq 1). So as to make comparisons with their metal complexes (see below) and the previously reported **11**,[86,87] **13**,[67] and **14**,[85] the X-ray structures of **15** and **16** were determined. The molecular structures and selected distances and angles are given in the Supporting Information (SI).

The solid-state molecular structures of **15** and **16** are comparable, and the geometries represent an arrangement that is reminiscent of that required to bind to a metal center (in terms of N(1) lone pair and N−H bond orientations). Similar arrangements were found previously for **13** and **14**.[67,85] Unexpectedly, there is no intra- or intermolecular hydrogen bonding present in either compound. In general terms, the bond lengths and angles lie within the expected ranges for compounds of these types.[88]

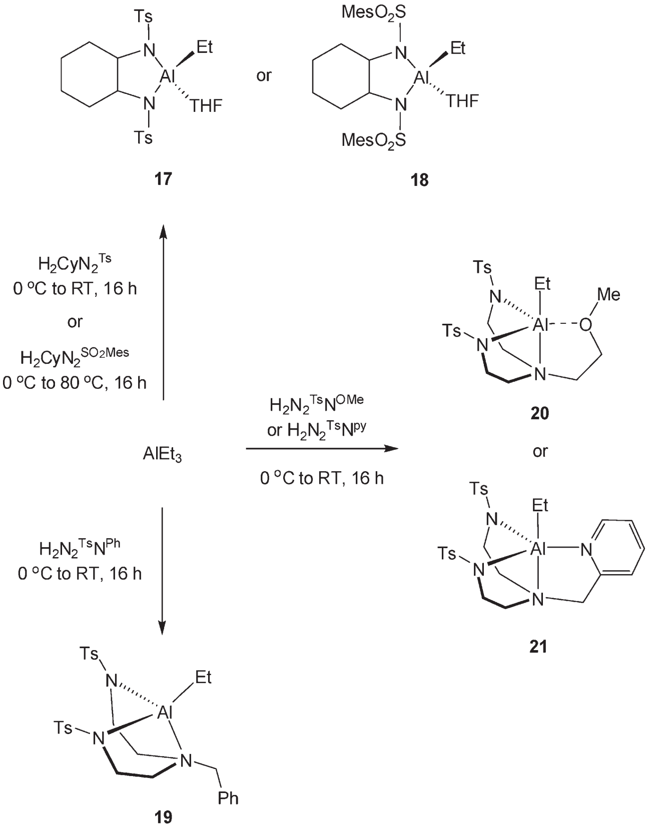


(1)

Initial complexation studies (Scheme 1) focused on alkyl complexes, which we hoped would act as intermediates en route to the more desirable alkoxide initiators via protonolysis reactions with alcohols, according to literature precedent.[89] Reactions of $AlEt_3$ with $H_2CyN_2^{Ts}$ (**11**) or $H_2CyN_2^{SO_2Mes}$ (**12**) in THF gave the four-coordinate Lewis base adducts $Al(CyN_2^{Ts})Et(THF)$ (**17**) and $Al(CyN_2^{SO_2Mes})Et(THF)$ (**18**), the latter reaction requiring heating at 80 °C. Reaction with $H_2N_2^{Ts}N^{Ph}$ (**15**) at room temperature in the same solvent gave the four-coordinate, THF-free $Al(N_2^{Ts}N^{Ph})Et$ (**19**), containing a tridentate bis(sulfonamide)amine ligand. Finally, reaction of $AlEt_3$ with $H_2N_2^{Ts}N^{OMe}$ (**13**) and $H_2N_2^{Ts}N^{py}$ (**14**) gave $Al(N_2^{Ts}N^{OMe})Et$ (**20**) and $Al(N_2^{Ts}N^{py})Et$ (**21**), also as THF-free complexes. The ^1H NMR shift of the 2-position hydrogen atom of the pyridyl donor of **21** (δ = 9.05 ppm) in CD_2Cl_2 is significantly shifted from that in the free ligand (δ = 8.58 ppm in the same solvent). This is consistent with coordination to Al, giving the five-coordinate geometry illustrated in Scheme 1. The isolated yields for **17**−**21** were in the range 55−70% after recrystallization. NMR tube scale monitoring of these reactions in C_6D_6 showed quantitative formation of the complexes.

The X-ray structures of compounds **17**−**21** have been determined and are compared in Figure 4. Selected distances and angles are listed in Tables 1−4. The solid-state structures are consistent with those proposed in Scheme 1 on the basis of solution NMR and other analytical data.

Scheme 1. Synthesis of the New Aluminum Ethyl Complexes 17−21[a]



[a] All reactions were carried out in THF.

Compounds **17** and **19** have approximately tetrahedral aluminum centers. Each Al is bonded to two tosyl amide nitrogens and one ethyl ligand, with no significant difference between the $Al{-}N_{Ts}$ and Al−C distances for the two compounds. In **17** the fourth coordination site is occupied by a THF ligand, whereas in **19** the tertiary nitrogen (N_{am}) of $N_2^{Ts}N^{Ph}$ fulfills this role. The aluminum in **20** is also approximately tetrahedral, with an additional long Al···O distance of 2.8305(14) Å to the pendant arm methoxy donor. The Al···O interaction barely perturbs the coordination sphere around Al, as judged by comparison with the $N_2^{Ts}N^{Ph}$ analogue **19**, bearing a noninteracting CH_2Ph arm. For example, for compound **19**, Al−C = 1.940(3) Å, $N_{am}{-}Al{-}C$ = 120.56(12)° and for compound **20**, Al−C = 1.949(2) Å, $N_{am}{-}Al{-}C$ = 126.84(8)°. In contrast, $Al(N_2^{Ts}N^{py})Et$ (**21**), featuring an additional pyridyl donor, has a distorted trigonal-bipyramidal geometry with an $Al{-}N_{py}$ distance (2.107(2) Å) within the expected range for a dative bond,[88] consistent with the solution ^1H NMR data mentioned above. The $N_{am}{-}Al{-}C$ angle has opened up to 156.74(8)° to accommodate the additional donor, and the Al−C (1.986(2) Å) and $Al{-}N_{Ts}$ (av 1.932(1) Å) distances are significantly longer than those in **17**, **19**, and **20** (range 1.940(3)−1.949(4) and 1.858(2)−1.895(2) Å, respectively).

Only two crystallographically characterized aluminum tosyl sulfonamide compounds have been reported previously, namely, **8** (Figure 2)[75] and *S*,*S*,*S*-Al{N(CH(Me)CH$_2$NTs)$_3$}.[73] Both have additional intramolecular S=O···Al interactions (as shown in Figure 2 for **8**) that are absent in **17**−**21**. There have also been a number of

---

(86) Nieger, M.; Josten, W.; Vogtle, F. *Private communication*, **2004**.

(87) Pritchett, S.; Gantzel, P.; Walsh, P. J. *Organometallics* **1999**, *18*, 823–831.

(88) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746 (The United Kingdom Chemical Database Service).

(89) Peng, K.-F.; Chen, C.-T. *Dalton Trans.* **2009**, 9800–9806.

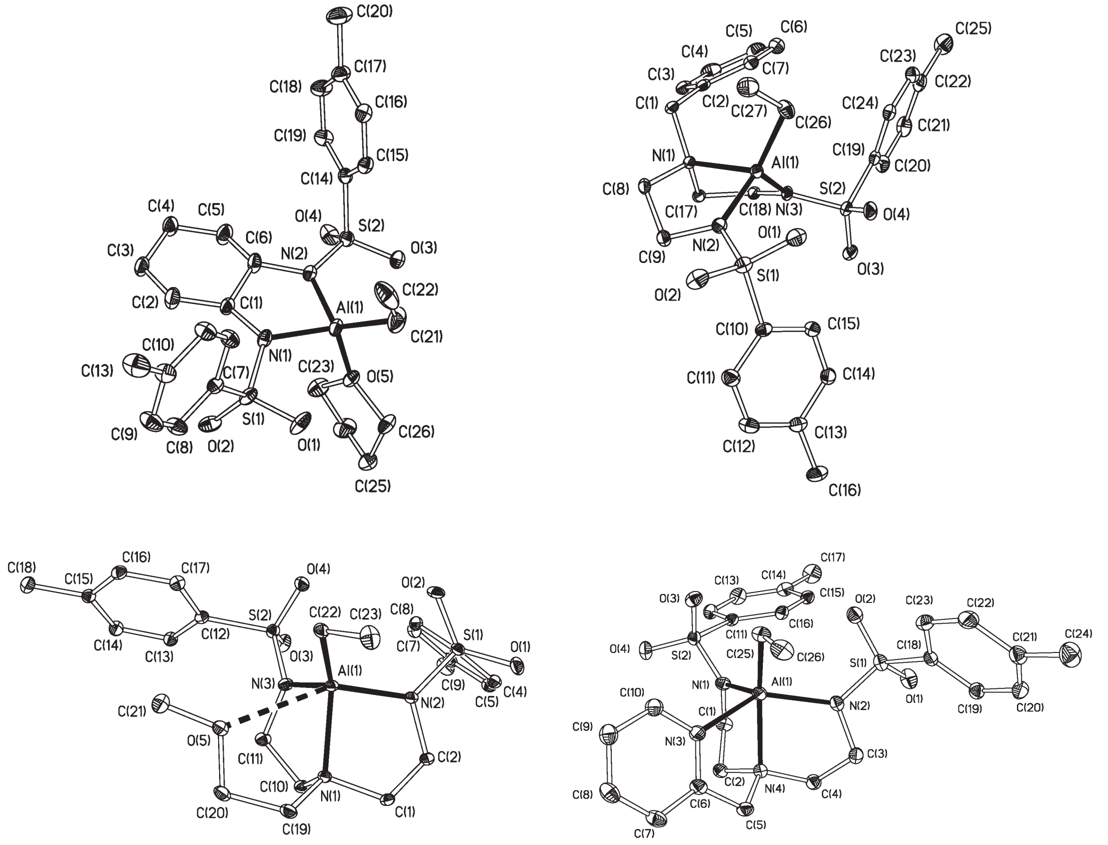


Figure 4. Displacement ellipsoid plots of Al(CyN$_2^{Ts}$)Et(THF) (**17**, top left), Al(N$_2^{Ts}$N^{Ph})Et (**19**, top right), Al(N$_2^{Ts}$N^{OMe})Et (**20**, bottom left), and Al(N$_2^{Ts}$N^{py})Et (**21**, bottom right). H atoms are omitted for clarity. Ellipsoids are drawn at the 20% probability level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Al(CyN$_2^{Ts}$)Et(THF) (17)

Al(1)−N(1)	1.867(3)	Al(1)−O(5)	1.858(2)
Al(1)−N(2)	1.872(3)	Al(1)−C(21)	1.949(4)
N(1)−Al(1)−N(2)	85.95(11)	N(1)−Al(1)−O(5)	106.74(12)
N(2)−Al(1)−O(5)	103.54(13)	N(1)−Al(1)−C(21)	123.58(19)
N(2)−Al(1)−C(21)	124.1(2)	O(5)−Al(1)−C(21)	109.47(17)

Table 2. Selected Bond Distances (Å) and Angles (deg) for Al(N$_2^{Ts}$N^{Ph})Et (19)

Al(1)−N(1)	2.023(2)	Al(1)−N(3)	1.858(2)
Al(1)−N(2)	1.864(2)	Al(1)−C(26)	1.940(3)
N(1)−Al(1)−N(2)	87.15(9)	N(1)−Al(1)−N(3)	86.37(9)
N(2)−Al(1)−N(3)	116.26(10)	N(1)−Al(1)−C(26)	120.56(12)
N(2)−Al(1)−C(26)	114.64(12)	N(3)−Al(1)−C(26)	122.80(12)

Table 3. Selected Bond Distances (Å) and Angles (deg) for Al(N$_2^{Ts}$N^{OMe})Et (20)

Al(1)−N(1)	2.035(1)	Al(1)−C(22)	1.949(2)
Al(1)−N(2)	1.895(2)	Al(1)···O(5)	2.830(1)
Al(1)−N(3)	1.860(2)		
N(1)−Al(1)−N(2)	86.06(6)	N(1)−Al(1)−N(3)	88.00(6)
N(2)−Al(1)−N(3)	112.34(7)	N(1)−Al(1)−C(22)	126.84(8)
N(2)−Al(1)−C(22)	112.11(7)	N(3)−Al(1)−C(22)	124.23(8)
N(1)−Al(1)···O(5)	67.38(5)	N(2)−Al(1)···O(5)	150.95(6)
N(3)−Al(1)···O(5)	79.54(6)	O(5)···Al(1)−C(22)	77.72(6)

Table 4. Selected Bond Distances (Å) and Angles (deg) for Al(N$_2^{Ts}$N^{py})Et (21)

Al(1)−N(1)	1.911(2)	Al(1)−N(4)	2.185(2)
Al(1)−N(2)	1.952(2)	Al(1)−C(25)	1.986(2)
Al(1)−N(3)	2.107(2)		
N(1)−Al(1)−N(2)	111.65(8)	N(1)−Al(1)−N(3)	101.95(7)
N(1)−Al(1)−N(4)	82.92(7)	N(2)−Al(1)−N(3)	133.77(8)
N(2)−Al(1)−N(4)	79.20(7)	N(3)−Al(1)−N(4)	74.31(7)
N(1)−Al(1)−C(25)	118.01(9)	N(2)−Al(1)−C(25)	100.26(9)
N(3)−Al(1)−C(25)	90.47(8)	N(4)−Al(1)−C(25)	156.74(8)

structures reported for aluminum complexes containing −N(R)SO_2CF_3 donors, including the four-coordinate alkyl complex **10** in Figure 2, which has a comparable geometry to **17**, **19**, and **20**.[76,77,79,90]

As mentioned, it was hoped that the new aluminum alkyls would serve as entry points to the corresponding alkoxide complexes, which are usually superior initiators for ROP. Unfortunately, reaction of **17**−**21** with either isopropyl or benzyl alcohol yielded mixtures of protio-ligand, residual metal alkyl, and Al(OR)$_3$ species in benzene at room temperature. Performing the reactions at low temperature in alternative solvents and/or at high dilution gave similar mixtures. Therefore, a different route to alkoxide complexes was sought. Drawing upon our previous work on titanium complexes where sulfonamide ligand protonolysis was also an issue,[67] we focused on reactions with mixed alkyl-alkoxide aluminum precursors of the type Al(OR)Et$_2$ (R = ^{i}Pr or Bn).[91,92]

Reaction of H$_2$CyN$_2^{Ts}$ (**11**) or H$_2$N$_2^{Ts}$N^{Ph} (**15**) with Al(OR)Et$_2$ (R = ^{i}Pr or Bn) led to complicated product

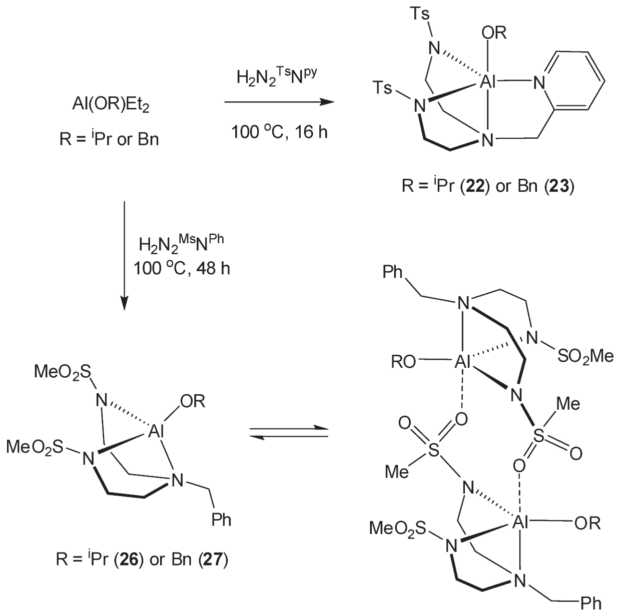
---

(90) Corey, E. J.; Sarshar, S.; Bordner, J. *J. Am. Chem. Soc.* **1992**, *114*, 7938–7939.

(91) Kunicki, A. R.; Pasynkiewicz, S.; Jankowski, J.; Mank, B. *Pol. J. Chem.* **2004**, *78*, 1857–1864.

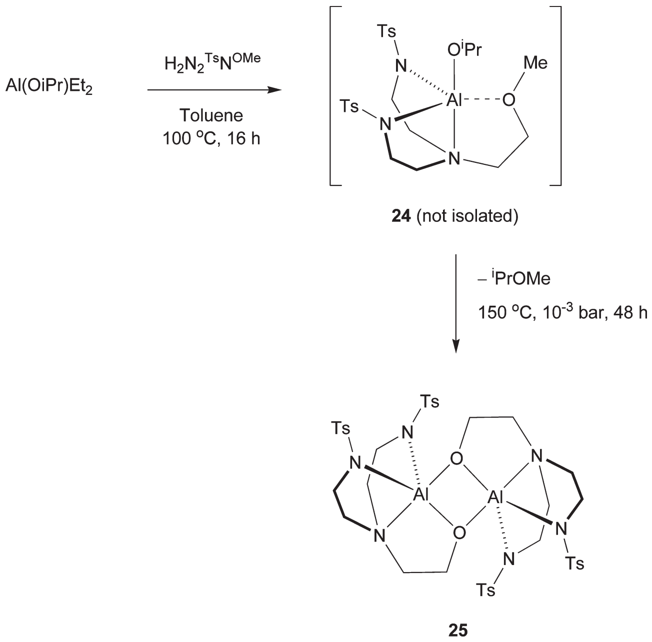
(92) Hirabayashi, T.; Sakakibara, T.; Ishii, Y. *J. Organomet. Chem.* **1972**, *35*, 19–25.

Scheme 2. Synthesis of the New Aluminum Alkoxide Complexes 22, 23, 26, and 27[a]



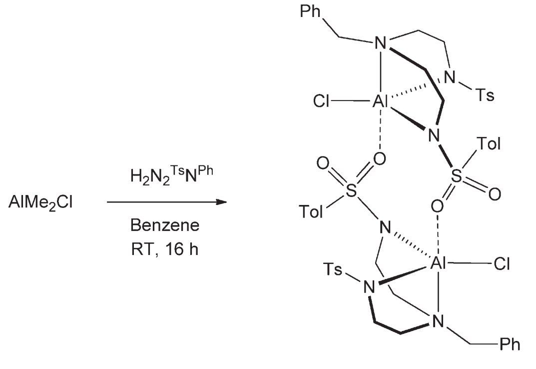
[a] Reactions were carried out in toluene.

Scheme 3. Ligand Demethylation Leading to [Al($N_2^{Ts}N^O$)]$_2$ (25)



mixtures, and no single product could be identified. The corresponding reaction for $H_2CyN_2^{SO_2Mes}$ (**12**) also gave a mixture of products, among which was Al($CyN_2^{SO_2Mes}$)Et(THF) (**18**), indicative of redistribution reactions. However, reaction of $H_2N_2^{Ts}N^{py}$ with Al(OR)Et_2 proceeded smoothly at 100 °C to give Al($N_2^{Ts}N^{py}$)(O^{i}Pr) (**22**) and Al($N_2^{Ts}N^{py}$)(OBn) (**23**) in ca. 65% isolated yield (Scheme 2). The NMR data for these compounds are in agreement with five-coordinate, C_s-symmetric aluminum compounds, as confirmed crystallographically for Al($N_2^{Ts}N^{py}$)Et (**21**). Surprisingly, reaction of $H_2N_2^{Ts}N^{OMe}$ (**13**) with Al(O^{i}Pr)Et_2 gave a mixture of products, among which appeared to be the desired alkoxide Al($N_2^{Ts}N^{OMe}$)O^{i}Pr (**24**, Scheme 3). However, attempted purification by crystallization afforded only the ligand-demethylated dimer [Al($N_2^{Ts}N^O$)]$_2$ (**25**, $N_2^{Ts}N^O$ = $OCH_2CH_2N(CH_2CH_2NTs)_2$) as colorless crystals. The ^{1}H and ^{13}C{^{1}H} NMR data and a preliminary X-ray structure determination (see Figure S1 in the SI) are consistent with the structure illustrated in Scheme 3. Compound **25** could be reproducibly synthesized in 49% overall yield by heating the crude initial mixture containing **24** at 150 °C under reduced pressure for 48 h.

In contrast to the mixtures formed with the tosylated protio-ligand **15**, reaction of $H_2N_2^{Ms}N^{Ph}$ (**16**, $-NSO_2Me$ substituted) with Al(OR)Et_2 gave Al($N_2^{Ms}N^{Ph}$)(O^{i}Pr) (**26**) and Al($N_2^{Ms}N^{Ph}$)(OBn) (**27**) in good yield (Scheme 2). NMR investigations of analytically pure samples in various solvents showed a mixture of monomeric and dimeric species in both cases. For example, in C_6D_6 the compounds exist as C_2-symmetric dimers with the $PhC\underline{H}_2N$ protons appearing as two mutually coupled doublets, consistent with S=O···Al bridging sulfone groups in a manner analogous to that for [Al($N_2^{Ts}N^{Ph}$)Cl]$_2$ (**28**, see below). In CD_2Cl_2, the spectra show a ca. 1:2 mixture of both dimeric and monomeric (C_s-symmetric, akin to Al($N_2^{Ts}N^{Ph}$)Et (**19**)) species, the latter being suggested by a singlet for the $PhC\underline{H}_2N$ protons. Addition of a few drops of pyridine-d_5 to the CD_2Cl_2 solution significantly simplified the spectra, which were consistent with the formation of Lewis base adducts Al($N_2^{Ms}N^{Ph}$)(OR)(pyridine-d_5).



28

(2)

Since reactions between $H_2N_2^{Ts}N^{Ph}$ and Al(OR)Et_2 gave intractable mixtures, alternative routes to the target alkoxides via the corresponding chloride complex were investigated. Reaction of $AlMe_2Cl$ with $H_2N_2^{Ts}N^{Ph}$ (**15**) gave [Al($N^{Ts}{}_2N^{Ph}$)Cl]$_2$ (**28**, eq 2) in 58% yield after recrystallization. The molecular structure is shown in Figure 5, and selected bond lengths and angles are given in Table 5. Compound **28** is an approximately C_2-symmetric, dimeric species formed though two bridging S=O···Al interactions (Al(1)−O(8) = 1.874(3) Å; Al(2)−O(4) = 1.854(2) Å), as has been observed previously,[76,90] Each Al has an approximately trigonal-bipyramidal geometry, with the Cl ligands and N_{Ts} donors occupying the equatorial positions. The Al−N_{Ts} distances in **28** (av 1.904(2) Å, range 1.892(3)−1.916(3) Å) lie in general within the ranges mentioned above. However, the Al−N_{Ts} distances associated with the bridging SO_2Tol groups (av 1.914(2) Å) are significantly longer than those for the nonbridging ones (av 1.894(2) Å). Similarly, the S=O···Al interactions significantly lengthen the tosyl S=O bonds (S(2,4)=O = 1.477(2) Å for the bridging oxygens vs av S(2,4)=O = 1.434(2) Å for the terminal ones).

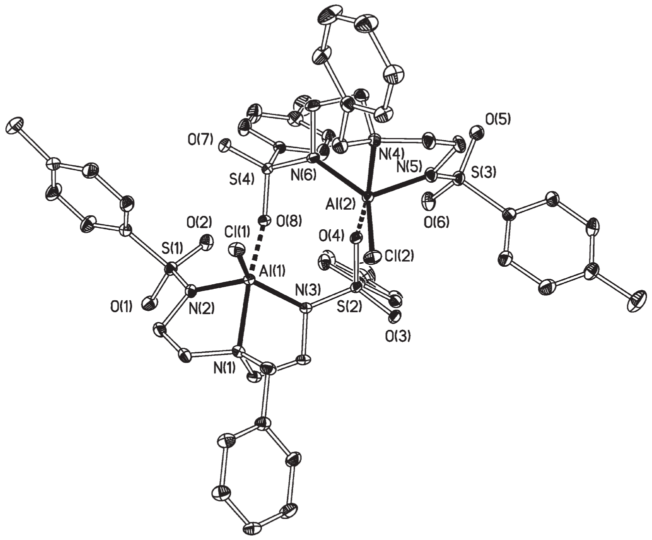


Figure 5. Displacement ellipsoid plot of $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (**28**). H atoms are omitted for clarity. Ellipsoids are drawn at the 20% probability level.

Table 5. Selected Bond Distances (Å) and Angles (deg) for $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (28)

Al(1)−N(1)	2.085(3)	Al(2)−N(4)	2.100(3)
Al(1)−N(2)	1.895(3)	Al(2)−N(5)	1.892(3)
Al(1)−N(3)	1.912(3)	Al(2)−N(6)	1.916(3)
Al(1)−O(8)	1.874(3)	Al(2)−O(4)	1.854(2)
Al(1)−Cl(1)	2.1775(14)	Al(2)−Cl(2)	2.1814(14)
S(2)−O(3)	1.435(3)	S(4)−O(7)	1.434(2)
S(2)−O(4)	1.477(2)	S(4)−O(8)	1.477(2)
N(1)−Al(1)−N(2)	81.68(13)	N(1)−Al(1)−N(3)	80.12(12)
N(1)−Al(1)−N(3)	118.95(13)	N(1)−Al(1)−O(8)	171.68(12)
N(2)−Al(1)−O(8)	99.63(12)	N(3)−Al(1)−O(8)	92.15(12)
N(1)−Al(1)−Cl(1)	93.08(9)	N(2)−Al(1)−Cl(1)	110.91(11)
N(3)−Al(1)−Cl(1)	127.78(10)	O(8)−Al(1)−Cl(1)	94.10(9)
N(4)−Al(2)−N(5)	82.15(13)	N(4)−Al(2)−N(6)	80.73(12)
N(5)−Al(2)−N(6)	118.79(14)	N(4)−Al(2)−O(4)	171.47(12)
N(5)−Al(2)−O(4)	100.28(13)	N(6)−Al(2)−O(4)	90.99(12)
N(4)−Al(2)−Cl(2)	92.57(9)	N(5)−Al(2)−Cl(2)	110.31(11)
N(6)−Al(2)−Cl(2)	128.72(10)	N(6)−Al(2)−Cl(2)	94.21(9)

It is interesting to contrast the monomeric nature of four-coordinate $Al(N_2{}^{Ts}N^{Ph})Et$ (**19**) with the dimeric one found for $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$. The difference can be attributed to the differences in electronegativity for the different ligands, Et and Cl. The solution ^1H and $^{13}C\{^1H\}$ NMR data for **28** are consistent with this structure being retained in solution, and the spectra are similar to those of the dimeric forms of the alkoxide analogues **26** and **27** (Scheme 2). Unfortunately, attempts to make alkoxide complexes analogous to **26** and **27** from **28** using LiOR (R = ^{i}Pr or Bn) were unsuccessful, again giving intractable mixtures of products.

In a further effort to stabilize well-defined monomeric alkoxide ROP initiators, reactions were undertaken using $Al(OCH_2CH_2NH_2)Et_2$.[93] This contains a potentially chelating amine functional group, which we hoped would confer additional stability on the target complexes. During the course of our studies we structurally characterized this known compound, and further details are given in the SI (see Figure S2 and the CIF).

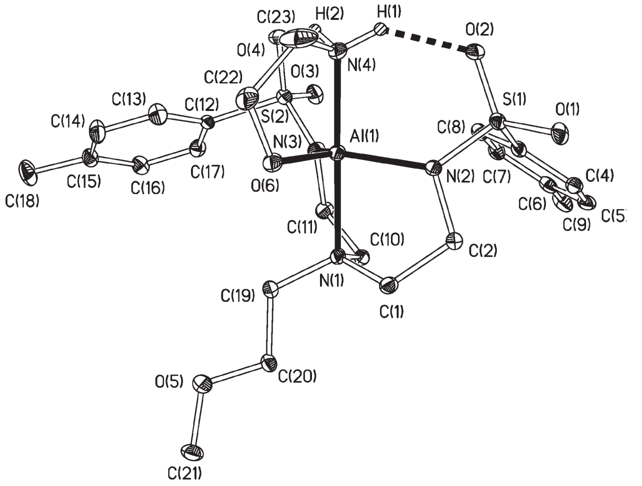
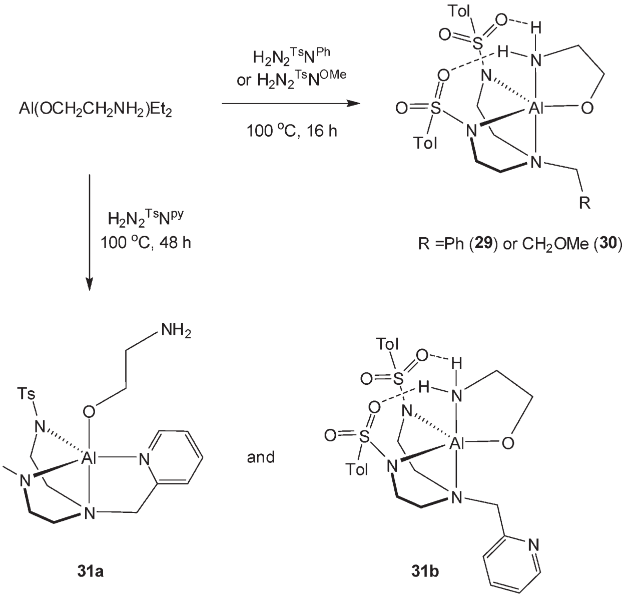


Figure 6. Displacement ellipsoid plot of $Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (**30**). C-bound H atoms are omitted for clarity. H(1) and H(2) are drawn as spheres of arbitrary radius. Ellipsoids are drawn at the 20% probability level.

Scheme 4. Synthesis of Aluminum Sulfonamide Complexes Bearing a 2-Aminoethoxide Ligand[a]



[a] All reactions were carried out in toluene.

As summarized in Scheme 4, heating toluene solutions of $Al(OCH_2CH_2NH_2)Et_2$ with $H_2N_2{}^{Ts}N^{Ph}$, $H_2N_2{}^{Ts}N^{OMe}$, or $H_2N_2{}^{Ts}N^{py}$ successfully gave the corresponding 2-aminoethoxide complexes $Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NH_2)$ (**29**), $Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (**30**), and $Al(N_2{}^{Ts}N^{py})(OCH_2CH_2NH_2)$ (**31**), respectively, in isolated yields of 68−79%. The product(s) of the corresponding reaction with $H_2CyN_2{}^{Ts}$ (**11**) gave broad and complicated spectra, which we were not able to confidently assign. The solid-state structure of **30** has been determined and is shown in Figure 6. Selected bond distances and angles are given in Table 6.

$Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (**30**) has a distorted trigonal-bipyramidal geometry and approximate C_s molecular symmetry. The anionic sulfonamide nitrogen and alkoxide oxygen donors occupy the equatorial positions, and the tertiary N_{am} of $N_2{}^{Ts}N^{OMe}$ and the NH_2 of the aminoethoxide

---

[93] Hurley, T. J.; Robinson, M. A.; Scruggs, J. A.; Trotz, S. I. *Inorg. Chem.* **1967**, *3*, 1310–1315.

Table 6. Selected Bond Distances (Å) and Angles (deg) for $Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (30)

Al(1)−N(1)	2.078(4)	O(2)···H(1)	1.95(7)
Al(1)−N(2)	1.917(4)	O(4)···H(2)	2.06(7)
Al(1)−N(3)	1.915(4)	S(1)−O(1)	1.448(4)
Al(1)−N(4)	2.006(5)	S(1)−O(2)	1.439(4)
Al(1)−O(6)	1.759(4)	S(2)−O(3)	1.441(4)
N(4)−H(1)	0.94(7)	S(3)−O(4)	1.443(4)
N(4)−H(2)	0.81(7)		
N(1)−Al(1)−N(2)	82.68(17)	N(1)−Al(1)−N(3)	83.30(17)
N(2)−Al(1)−N(3)	114.82(19)	N(1)−Al(1)−N(4)	175.4(2)
N(2)−Al(1)−N(4)	95.8(2)	N(3)−Al(1)−N(4)	101.3(2)
N(1)−Al(1)−O(6)	90.71(17)	N(2)−Al(1)−O(6)	120.65(19)
N(3)−Al(1)−O(6)	122.83(19)	N(4)−Al(1)−O(6)	86.3(2)

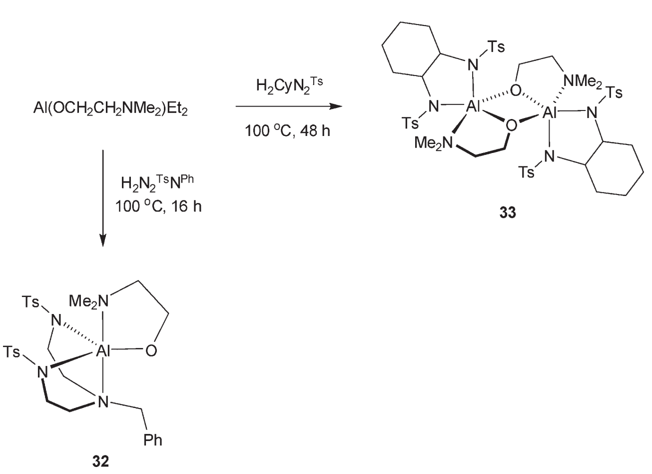
take up the axial positions, the latter having comparable bond lengths ($Al-N_{am}$ = 2.078(4); $Al-NH_2$ = 2.006(5) Å). The OMe donor of the pendant arm is not coordinated, displaced in preference for NH_2 coordination (the primary amine being the more effective Lewis base). In addition, amine coordination is supplemented by intramolecular hydrogen bonding between the NH_2 hydrogens and two adjacent sulfonamide oxygen atoms. The $NH\cdots O_{Ts}$ distances of 1.95(7) and 2.06(7) Å are within the expected ranges for such interactions.[88,94] The IR spectrum of **30** shows ν(N−H) bands at 3306 and 3268 cm^{-1}, which are shifted to lower frequency compared to those in the starting compound $Al(OCH_2CH_2NH_2)Et_2$ (ν(N−H) = 3356 and 3287 cm^{-1}), which has a chelating $OCH_2CH_2NH_2$ ligand but no $NH\cdots O$ hydrogen bonds (SI, Figure S2). There is no significant differences in length between the S=O bonds engaged in hydrogen bonding (S(1)−O(2), S(2)−O(4)) and those that are not. The $Al-N_{Ts}$ distances (1.917(4) and 1.915(4) Å) are slightly shorter than those in $Al(N_2{}^{Ts}N^{py})Et$ (**21**, av 1.932(1) Å) and very similar to those for $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (**28**) (av 1.904(2) Å).

The IR spectrum of $Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NH_2)$ (**29**) has similar ν(N−H) bands (3308 and 3262 cm^{-1}) to those of **30**, and a similar structure is proposed (Scheme 4). Note that in the otherwise identical $Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**32**, see below), which has a NMe_2 donor in place of NH_2, these bands are absent. The ^1H and $^{13}C\{^1H\}$ NMR spectra of **29** and **30** are comparable and relatively simple, and consistent with the presence of one five-coordinate, C_s-symmetric isomer in solution in each case.

In contrast, the IR spectrum of $Al(N_2{}^{Ts}N^{py})(OCH_2CH_2NH_2)$ (**31**) shows at least four ν(N−H) bands in the range 3320−3160 cm^{-1}, and the solution ^1H and $^{13}C\{^1H\}$ NMR spectra suggest a mixture of two isomers, **31a** (major) and **31b** (minor), in a ca. 2:1 ratio. Both isomers have C_s symmetry and the same composition "$Al(N_2{}^{Ts}N^{py})(OCH_2CH_2NH_2)$" according to integration, consistent with the satisfactory elemental analysis for bulk samples of **31**. The ^1H NMR shift of the 2-position hydrogen atom of the pyridyl donor in the major isomer appears at δ = 8.87 ppm, consistent with coordination to Al,[67] whereas the shift of δ = 8.52 ppm for the minor isomer is very close to that of the free $H_2N_2{}^{Ts}N^{py}$ in CD_2Cl_2 (δ = 8.58 ppm). We interpret these data in terms of the structures proposed in Scheme 4, with the pendant pyridyl and NH_2 donors competing for the vacant coordination site at Al.

As described below, the use of an aminoethoxide moiety in **29**−**31** appeared to lead to poor performance with regard to the controlled ROP of *rac*-LA. To probe these aspects, we prepared some representative complexes containing a 2-*N*,*N*-dimethylaminoethoxide ligand (Scheme 5), in effect replacing $-NH_2$ with $-NMe_2$. Reaction of $H_2N_2{}^{Ts}N^{Ph}$ with $Al(OCH_2CH_2NMe_2)Et_2$[93] gave monomeric $Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**32**). The NMR spectra for **32** were consistent with the five-coordinate structure proposed in Scheme 5, which is analogous to those of **29**, **30**, and **31b**, but without the intramolecular hydrogen bonding. The spectra indicated molecular C_s symmetry (e.g., equivalent SO_2Tol substituents and NMe_2 methyl groups), and NOE (nuclear Overhauser effect) experiments confirmed the *trans* arrangement of the tertiary N_{am} and NMe_2 donors, together with coordination of NMe_2 to Al.

Scheme 5. Synthesis of Aluminum Sulfonamide Complexes Bearing a $OCH_2CH_2NMe_2$ Ligand[a]



[a] All reactions were carried out in toluene.

Whereas reaction of $H_2CyN_2{}^{Ts}$ with $Al(OCH_2CH_2NH_2)Et_2$ gave rather ill-defined materials (see above), reaction with $Al(OCH_2CH_2NMe_2)Et_2$ formed "$Al(CyN_2{}^{Ts})(OCH_2CH_2NMe_2)$" (**33**) in 85% isolated yield. The NMR spectra for **33** are more complicated than would be expected for a C_s-symmetric, four-coordinate monomer analogous to $Al(CyN_2{}^{Ts})Et(THF)$ and $Al(CyN_2{}^{SO_2Mes})Et(THF)$ (Scheme 1), showing, for example, inequivalent SO_2Tol substituents and NMe_2 methyl groups. We propose that **33** possesses the dimeric structure shown in Scheme 5. A number of related dimeric aluminum complexes containing a $OCH_2CH_2NMe_2$ or related 2-aminoethoxide ligand in the arrangement shown for **33** have been structurally authenticated,[88] including $Al(OCH_2CH_2NH_2)Et_2$ (SI, Figure S2).

Polymerization Studies: Solution ROP of *rac*-LA. The series of complexes $Al(N_2{}^{Ts}N^R)Et$ (R = Ph (**19**) or py (**21**)), $Al(N_2{}^{Ts}N^{py})(OR')$ (R′ = ^{i}Pr (**22**) or Bn (**23**)), $Al(N_2{}^{Ms}N^{Ph})(OR')$ (R′ = ^{i}Pr (**26**) or Bn (**27**)), $Al(N_2{}^{Ts}N^R)(OCH_2CH_2NH_2)$ (R = Ph (**29**), OMe (**30**), or py (**31**)), $Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**32**), and $Al(CyN_2{}^{Ts})(OCH_2CH_2NMe_2)$ (**33**) allowed the systematic evaluation of the effects of sulfonamide ligand coordination number and N-substituents and initiating group type (Et, "simple" alkoxide, or 2-aminoethoxide). Each was assessed for its ROP performance for *rac*-LA. ROP experiments were performed in toluene at 70 °C ($[rac\text{-LA}]_0$:[Al] = 100:1), and under these conditions all the complexes were found to be active. The progress of each was monitored by regular sampling, and the results summarized in Table 7 correspond to 72 h reaction time (see the SI for other data). The molecular weights

---

[94] Aullón, G.; Bellamy, D.; Orpen, A. G.; Brammer, L.; Bruton, E. A. *Chem. Commun.* **1998**, 653–654.

Table 7. Solution Polymerization of *rac*-LA by $Al(N_2^{Ts}N^{Ph})Et$ (19), $Al(N_2^{Ts}N^{py})Et$ (21), $Al(N_2^{Ts}N^{py})(O^iPr)$ (22), $Al(N_2^{Ts}N^{py})(OBn)$ (23), $Al(N_2^{Ms}N^{Ph})(O^iPr)$ (26), $Al(N_2^{Ms}N^{Ph})(OBn)$ (27), $Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NH_2)$ (29), $Al(N_2^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (30), $Al(N_2^{Ts}N^{py})(OCH_2CH_2NH_2)$ (31), $Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (32) and $Al(CyN_2^{Ts})(OCH_2CH_2NMe_2)$ (33)[a]

entry	catalyst	conversion (%)[b]	k_{app} (h^{-1})	M_n (GPC)[c]	M_n (calcd)[d]	M_w/M_n
1	$Al(N_2^{Ts}N^{Ph})Et$ (**19**)	20	[e]	18 320	2910	1.47
2	$Al(N_2^{Ts}N^{py})Et$ (**21**)	48	[e]	13 060	8870	1.73
3	$Al(N_2^{Ts}N^{py})(O^iPr)$ (**22**)	83	0.0245(5)	19 480	12 010	1.11
4	$Al(N_2^{Ts}N^{py})(OBn)$ (**23**)	87	0.0280(8)	14 270	12 610	1.14
5	$Al(N_2^{Ms}N^{Ph})(O^iPr)$ (**26**)	81	0.0230(4)	16 040	11 690	1.12
6	$Al(N_2^{Ms}N^{Ph})(OBn)$ (**27**)	76	0.0203(7)	16 340	11 690	1.12
7	$Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NH_2)$ (**29**)	96[f]	[f]	27 150	13 790	1.44
8	$Al(N_2^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (**30**)	96[f]	[f]	25 060	13 860	1.45
9	$Al(N_2^{Ts}N^{py})(OCH_2CH_2NH_2)$ (**31**)	93[f]	[f]	24 770	13 400	1.44
10	$Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**32**)	82	0.0235(11)	16 960	11 890	1.12
11	$Al(CyN_2^{Ts})(OCH_2CH_2NMe_2)$ (**33**)	76	0.0202(8)	30 460	10 740	1.22

[a] Conditions: $[rac\text{-}LA]_0$:[Al] = 100:1, 4.0 mL of toluene at 70 °C. See Experimental Section for other details. [b] % conversion by NMR at 72 h reaction time. [c] Molecular weights (g mol^{-1}) determined by GPC in THF at 30 °C using the appropriate Mark–Houwink corrections. [d] Expected M_n (g mol^{-1}) for 1 chain growing per metal center. [e] Not measured due to the poor conversion and sluggish behavior. [f] Polymerization terminated after 72 h, and k_{app} not measured due to gel formation after ca. 18 h.

and PDIs (M_w/M_n) were determined by gel permeation chromatography (GPC) using the appropriate Mark–Houwink corrections for PLA.[95–97] Polymerization using these aluminum complexes required extended reaction times compared to the sulfonamide-supported zirconium analogues we reported previously.[67] For example the zirconium alkoxide catalyst based upon $N_2^{Ts}N^{OMe}$ achieved 94% conversion of 100 equiv of *rac*-LA after ca. 6 h, while **30** reached 96% conversion only after 72 h. This observation is in agreement with the literature. For example, bis(phenolate) complexes of zirconium demonstrate enhanced activity compared to similar aluminum species.[63,65,68] This is due to the smaller radius of aluminum.

The ethyl complexes **19** and **21** (entries 1 and 2, Table 7) were found to be active but with relatively low conversions and poor control. Only ca. 20–50% of the *rac*-LA had been polymerized after 72 h, and the polymers formed had broad PDIs (ca. 1.5–1.7) indicative of a poorly controlled process. The MALDI-ToF mass spectra of the polymers were complex and showed the presence of both cyclic poly(*rac*-LA) and linear chains terminated by EtC(O)CH(Me)O– end groups, the latter forming as a result of insertion of *rac*-LA into the Al–Et of the initiator. The M_n values measured by GPC were substantially higher than predicted on the basis of conversion (judged by ^1H NMR analysis of the reaction mixtures) and assuming each aluminum center is catalytically active. This deviation is consistent with poor rates of initiation (LA insertion into the Al–Et bond) compared to propagation (insertion into the Al–O bond of the so-formed Al–$\{OCH(Me)C(O)\}_n$–Et growing chains), which is a well-established feature of metal alkyl initiators.[98,99]

In contrast to **19** and **21**, the alkoxides complexes **22**–**27** were considerably better behaved (entries 3–6, Table 7). The polymerization experiments were monitored at 6, 24, 48, and 72 h intervals, and representative plots concerning the kinetic aspects and control of M_n and PDI are given in Figures 7 and 8 (see the SI for other plots). All gave first-order consumption of *rac*-LA and a well-controlled polymerization process, as evidenced by narrow PDIs and a linear

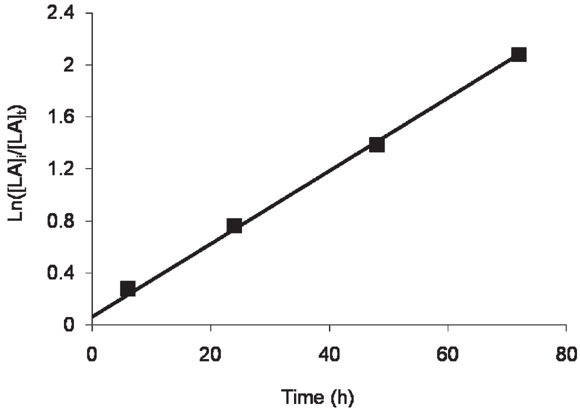


Figure 7. First-order plot for *rac*-LA consumption using $Al(N_2^{Ts}N^{py})(OBn)$ (**23**). Conditions: $[rac\text{-}LA_0]$:[**23**] = 100:1, 4 mL of toluene, 70 °C, 0.1 mL aliquots taken at the given intervals. See Experimental Section for other details. Linear fit (r^2 = 0.997). See the SI for corresponding plots for **22**, **26**, **27**, **32**, and **33**.

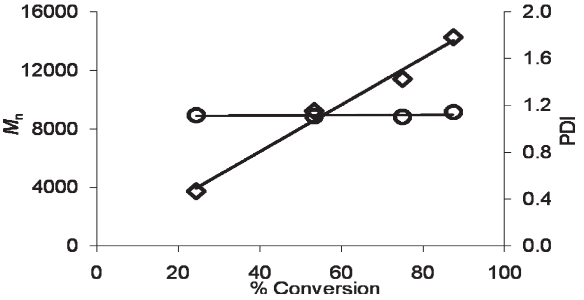


Figure 8. Plots of M_n and PDI (determined by GPC) vs conversion for the polymerization of *rac*-LA using $Al(N_2^{Ts}N^{py})$(OBn) (**23**). Conditions: $[rac\text{-}LA_0]$:[**23**] = 100:1, 4 mL of toluene, 70 °C, 0.1 mL aliquots taken at the given intervals. Hollow diamonds correspond to M_n and hollow circles to PDI. See the SI for corresponding plots for **22**, **26**, **27**, **29**, and **31**–**33**.

---

(95) Rudin, A.; Hoegy, H. L. W. *J. Polym. Sci., Part A: Polym. Chem.* **1972**, *10*, 217–235.

(96) Barakat, I.; Jérôme, R.; Teyssié, P. h. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 505–514.

(97) Dorgan, J. R.; Janzen, J.; Knauss, D. M.; Hait, S. B.; Limoges, B. R.; Hutchinson, M. H. *J. Polym. Sci., Part B: Polym. Phys.* **2005**, *43*, 3100–3111.

(98) Gong, S.; Ma, H. *Dalton Trans.* **2008**, 3345–3357.

(99) Alonso-Moreno, C.; Garcas, A.; Sanchez-Barba, L. F.; Fajardo, M.; Fernandez-Baeza, J.; Otero, A.; Lara-Sanchez, A.; Antiaolo, A.; Broomfield, L.; Lapez-Solera, M. I.; Rodraguez, A. M. *Organometallics* **2008**, *27*, 1310–1321.

Table 8. Solvent-Free (melt) Polymerization of *rac*-LA by Al($N_2{}^{Ts}N^{Ph}$)Et (19), Al($N_2{}^{Ts}N^{py}$)Et (21), Al($N_2{}^{Ts}N^{py}$)(O^iPr) (22), Al($N_2{}^{Ts}N^{py}$)(OBn) (23), Al($N_2{}^{Ms}N^{Ph}$)(O^iPr) (26), Al($N_2{}^{Ms}N^{Ph}$)(OBn) (27), Al($N_2{}^{Ts}N^{Ph}$)($OCH_2CH_2NH_2$) (29), Al($N_2{}^{Ts}N^{OMe}$)($OCH_2CH_2NH_2$) (30), Al($N_2{}^{Ts}N^{py}$)($OCH_2CH_2NH_2$) (31), and Al($N_2{}^{Ts}N^{Ph}$)($OCH_2CH_2NMe_2$) (32)[a]

entry	catalyst	yield (%)[b]	M_n (GPC)[c]	M_n (calcd)[d]	M_w/M_n
1	Al($N_2{}^{Ts}N^{Ph}$)Et (**19**)	80	41 430	34 600	1.44
2	Al($N_2{}^{Ts}N^{py}$)Et (**21**)	75	37 390	32 540	1.47
3	Al($N_2{}^{Ts}N^{py}$)(O^iPr) (**22**)	83	41 150	35 900	1.21
4	Al($N_2{}^{Ts}N^{py}$)(OBn) (**23**)	79	34 310	34 160	1.20
5	Al($N_2{}^{Ms}N^{Ph}$)(O^iPr) (**26**)	94	35 480	40 490	1.60
6	Al($N_2{}^{Ms}N^{Ph}$)(OBn) (**27**)	95	36 710	40 920	1.53
7	Al($N_2{}^{Ts}N^{Ph}$)($OCH_2CH_2NH_2$) (**29**)	91	36 540	31 100	1.30
8	Al($N_2{}^{Ts}N^{OMe}$)($OCH_2CH_2NH_2$) (**30**)	81	35 000	34 870	1.52
9	Al($N_2{}^{Ts}N^{py}$)($OCH_2CH_2NH_2$) (**31**)	87	29 640	29 650	1.45
10	Al($N_2{}^{Ts}N^{Ph}$)($OCH_2CH_2NMe_2$) (**32**)	46	16 440	19 700	1.37

[a] Conditions: [*rac*-LA]$_0$:[Al] = 300:1 at 130 °C. See Experimental Section for other details. [b] % conversion by NMR at 2 h reaction time. [c] Molecular weights (g mol^{-1}) determined by GPC in THF at 30 °C using the appropriate Mark−Houwink corrections. [d] Expected M_n (g mol^{-1}) for 1 chain growing per metal center.

relationship between experimental M_n and % conversion. The gradients of the M_n versus % conversion plots were 237(13), 161(8), 208(10), and 220(6) g mol^{-1} (% conversion)$^{-1}$, respectively, which are higher than that expected (144.1 g mol^{-1} (% conversion)$^{-1}$ for [*rac*-LA]$_0$:[Al] = 100:1) for one poly(*rac*-LA) chain growing per metal center. This suggests that not all of the initiating (L)AlOR′ species have entered the catalytic cycle, perhaps due to some instability of the precatalysts (initiators) under the reaction conditions. Once polymerization is underway, the linear first-order kinetic plots (e.g., Figure 7) and linear M_n versus conversion (e.g., Figure 8) all suggest a stable catalyst system. Among these four catalysts, **23** gave the closest agreement between experimental M_n and that expected. The PDI of 1.14 and the linear relationship between M_n and % conversion (Figure 8, gradient 161(8) g mol^{-1} (% conversion)$^{-1}$) are also indicative of a well-controlled living-type behavior.

The apparent propagation rate constants (k_{app}) for pairs of initiators supported by the same ancillary ligand ($N_2{}^{Ts}N^{py}$ for **22** and **23**; $N_2{}^{Ms}N^{Ph}$ for **26** and **27**) had very similar values, as would be expected since they lead to the same propagating catalyst. Surprisingly, the values of k_{app} for catalysts based on tetradentate $N_2{}^{Ts}N^{py}$ (**22** and **23**, av 0.0263 h^{-1}) are slightly larger than those containing the tridentate $N_2{}^{Ms}N^{Ph}$ (**26** and **27**, av 0.0217 h^{-1}). A higher rate might have been expected for the $N_2{}^{Ms}N^{Ph}$-supported systems since access of *rac*-LA to the metal should be more facile. One explanation could be that the tetradentate homologue is more able to support a monomeric (and presumably more active) active species (L)Al-OR (R = poly(*rac*-LA) chain), whereas the tridentate $N_2{}^{Ms}N^{Ph}$ might lead to a higher equilibrium concentration of dormant binuclear complexes with, for example, bridging sulfonyl groups (as in **26**, **27**, or **28**) or a poly(*rac*-LA) chain (cf. the bridging OR group in **25** or **33**).

The ^{1}H NMR and MALDI-ToF mass spectra confirmed the presence of alkoxide-terminated poly(*rac*-LA). Disappointingly, all of the polymers produced were atactic according to the selectively homonuclear-decoupled NMR spectra. Examination of the MALDI-ToF mass spectra showed a Δ(*m*/*z*) separation of 72 between the polymer chains (i.e., one-half of a LA unit, 144.1 amu) consistent with extensive transesterification during the polymerization process. This and the high temperatures required for polymerization (which would be detrimental to any chain-end control of monomer insertion) are possible contributors to the lack of control of polymer tacticity in these systems.

Whereas the alkoxides **22**−**27** led to well-behaved ROP, analogous experiments using the 2-aminoalkoxide analogues Al($N_2{}^{Ts}N^R$)($OCH_2CH_2NH_2$) (**29**−**31**; entries 7−9, Table 7) all gave higher than predicted M_n values, larger PDIs, and, ultimately, gel formation after ca. 18 h reaction time. In contrast, use of the 2-*N*,*N*-dimethylaminoethoxide Al($N_2{}^{Ts}N^{Ph}$)($OCH_2CH_2NMe_2$) (**32**, entry 10, Table 7) once again gave reasonably well-controlled ROP, as judged by a better agreement between experimental and predicted M_n, a narrow PDI, and linear increase of M_n with conversion (SI, Figure S20). The k_{app} for **32** (0.0235(11) h^{-1}) was experimentally the same as those of the related Al($N_2{}^{Ts}N^{Ph}$)(OR′) systems **26** and **27** (0.0230(4) and 0.0203(7) h^{-1}), as expected for virtually identical propagating species. The MALDI-ToF mass spectrum of the polymer obtained using **32** confirmed the presence of the $OCH_2CH_2NMe_2$ end groups. The spectrum again showed a Δ(*m*/*z*) separation of 72 between the polymer chains, consistent with extensive transesterification.

We propose two explanations for the unusual behavior of **29**−**31**, both based on the presence of the terminal $-NH_2$ group. First, as seen in the structures (Scheme 4), the aminoethoxide ligand is strongly chelating to the aluminum center, augmented by two NH···O=S hydrogen bonds. Conceivably this could lead to sluggish initiation compared to the "normal" alkoxides **22**−**27** and **32**, the latter having a less Lewis basic $-NMe_2$ donor and no supporting hydrogen bonds. Second, the terminal $-NH_2$ group of the growing polymeryl chain in Al($N_2{}^{Ts}N^R$){poly(*rac*-LA)}-OCH_2CH_2-NH_2 may also be able to co-initiate the ROP of another *rac*-LA through an activated monomer process.[100] Such a process could lead to cross-linking and gel formation.

Catalyst **33** gives a linear relationship between M_n and monomer conversion with narrow PDIs (∼1.2) throughout the polymerization. Disappointingly, it was again observed that the experimental M_n was much higher than predicted, possibly consistent with sluggish initiation compared to propagation. The dimeric nature proposed for **33**, with a bridged-chelating Al(μ-$OCH_2CH_2NMe_2$)$_2$Al core, could likely account for this.

Polymerization Studies: ROP of *rac*-LA under Solvent-Free (Melt) Conditions. Catalysts **19**, **21**−**23**, **26**, **27**, and **29**−**32** were also assessed for their capabilities toward the ROP of *rac*-LA at 130 °C for 2 h ([*rac*-LA]$_0$:[Al] = 300:1) under

---

(100) Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. *Chem. Commun.* **2010**, *46*, 273−275.

industrially relevant solvent-free (melt) conditions. The results are summarized in Table 8.

The best-performing initiators from the solution-state studies, namely, the nonchelating alkoxides **22**, **23**, **26**, and **27** (entries 3−6), performed well under the more demanding, higher temperature melt conditions. Conversions of between ca. 80% and 95% with good agreements between found and calculated M_n values and reasonable PDIs were found (PDIs under melt conditions are typically broader than for the corresponding solution phase studies[67]). In particular the initiators supported by the tetradentate $N_2^{Ts}N^{py}$ ligand (**22** and **23**) gave poly(*rac*-LA) with a narrow PDI of ca. 1.2. The agreement between found and calculated M_n was especially good for **23**, mirroring the excellent performance of this complex in the solution phase (Table 7). Good M_n control and a reasonable PDI were also achieved with the 2-*N*,*N*-dimethylaminoethoxide species $Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (**32**, entry 10).

Surprisingly, both of the ethyl aluminum complexes **19** and **21** (entries 1 and 2) gave significantly improved ROP in the melt. The extents of conversion and PDIs of the poly(*rac*-LA) were comparable to those achieved with the alkoxides after 2 h, and there was reasonable agreement between the experimental and calculated M_n data. Similarly, catalysts **29**−**31** also gave much-improved performance in terms of molecular weight control and molecular weight distributions, with the $N_2^{Ts}N^{py}$-supported system **31** providing the best agreement between measured and calculated M_n. The origins of this difference are not fully clear. We tentatively speculate that the more forcing conditions and higher lactide concentration under melt conditions may help overcome the kinetic limitations associated with insertion into the Al−Et bonds of **19** and **21** or opening up the chelating aminoethoxide−aluminum chelate rings of **29**−**31**. Further work on other aluminum alkyl catalysts under melt conditions will be required to confirm this hypothesis.

Conclusion

We have reported the first comprehensive study of the synthesis, structures, and *rac*-LA ROP capability of sulfonamide-supported aluminum complexes. Both previously reported and new protio-ligands reported herein reacted readily with $AlEt_3$ to form $Al(CyN_2^R)Et(THF)$ (R = Ts or SO_2Mes) and $Al(N_2^{Ts}N^R)Et$ (R = Ph, OMe, or py). Corresponding reactions with $Al(OR')Et_2$ (R′ = ^iPr, Bn, $CH_2CH_2NH_2$, or $CH_2CH_2NMe_2$) gave $Al(N_2^{Ts}N^{py})(OR')$, $Al(N_2^{Ms}N^{Ph})(OR')$, $Al(N_2^{Ts}N^R)(OCH_2CH_2NH_2)$ (R = Ph, OMe, or py), $Al(N_2^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$, and $Al(CyN_2^{Ts})(OCH_2CH_2NMe_2)$. In general all of the above syntheses were straightforward, although reaction of $Al(O^iPr)Et_2$ with $H_2N_2^{Ts}N^{OMe}$ led to O-demethylation of the sulfonamide ligand. The X-ray structures of eight sulfonamide complexes showed a variety of four- and five-coordinate structures depending on the sulfonamide ligand and/or additional ligand (ethyl, chloride, 2-aminoethoxide).

Detailed comparison of solution ROP results with those in the literature should be undertaken with caution because of differences in experimental conditions such as temperature, solvent type, monomer:initiator ratio, and concentration. Generally speaking, however, the activity and molecular weight control achieved by the sulfonamide-supported catalysts compare well with literature results in the solution phase.[63]

Since most melt ROP experiments are usually carried out in the range 120−150 °C in very similar ways, this allows a more precise comparison of our results with those reported previously. Feijen's complex **3** (Figure 1) polymerizes 400 equiv of *rac*-LA to 95% conversion in the melt over 2 days at 130 °C.[54] The κ^2-bound sulfonamide complex **7** (Figure 2) is also active under melt conditions, although still requires fairly long reaction times (90% conversion after 10 h at 130 °C). The isotactic poly(lactide) formed has modest PDI values of ca. 1.5, but there is poor control of molecular weight.[74] Carpentier's aluminum complexes of salen-like ligands polymerize 400 equiv of *rac*-LA at 120 °C to 87% conversion after 0.5 h. The so-formed isotactic poly(lactide) had moderate to broad PDIs (1.4−1.9), but poor agreement was found between found and expected molecular weight.[101] Our results (Table 8) compare favorably with these examples. High conversions of up to 95% within 2 h reaction time were achieved, along with excellent control in the case of catalyst **23**, as judged by the close agreement between experimental and calculated M_n and narrow PDI. However, further iterations of ligand design will be required to find catalysts capable of achieving stereochemical control (e.g., high levels of heterotactic enrichment) either under solution or melt ROP conditions.

Experimental Section

General Methods and Instrumentation. All manipulations were carried out using standard Schlenk line or drybox techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over sodium (C_6H_6) or P_2O_5 ($CDCl_3$ and CD_2Cl_2), distilled under reduced pressure, and stored under dinitrogen in Teflon valve ampules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (^1H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two-dimensional $^1H-^1H$ and $^{13}C-^1H$ NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 ESP FTIR spectrometer. Samples were prepared in a drybox as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}). Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University.

MALDI-ToF mass spectra were measured using a Waters MALDI micro equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. The polymer samples were dissolved in THF at a concentration of 1 mg mL^{-1}. The cationization agent used was potassium trifluoroacetate (Fluka, > 99%) dissolved in THF at a concentration of 5 mg mL^{-1}. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL^{-1}. Solutions of matrix, salt, and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the refectron mode. Polymer molecular weights (M_n, M_w) were

---

(101) Bouyahyi, M.; Grunova, E.; Marquet, N.; Kirillov, E.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F. *Organometallics* **2008**, *27*, 5815–5825.

determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min^{-1}. Linear polystyrenes were used as primary calibration standards, and Mark−Houwink corrections for poly(*rac*-LA) in THF were applied for the experimental samples.[95−97]

Starting Materials. $H_2CyN_2^{Ts}$ (**11**),[82] $H_2CyN_2^{SO_2Mes}$ (**12**),[83] $H_2N_2^{Ts}N^{OMe}$ (**13**),[84] $H_2N_2^{Ts}N^{py}$ (**14**),[85] *N*-mesylaziridine,[102] $Al(O^iPr)Et_2$,[91,92] $Al(OBn)Et_2$,[91,92] $Al(OCH_2CH_2NH_2)Et_2$,[93] and $Al(OCH_2CH_2NMe_2)Et_2$[93] were synthesized according to published procedures. *rac*-LA was recrystallized twice from toluene and then sublimed twice prior to use. Other reagents were purchased from Sigma-Aldrich and used without further purification.

$H_2N_2^{Ts}N^{Ph}$ (15). To a slurry of tosylaziridine (4.93 g, 0.025 mol) in EtOH (250 mL) was added dropwise benzylamine (1.4 mL, 0.013 mol). The reaction mixture was stirred for 24 h at 35 °C, after which time volatiles of the resulting brown mixture were removed under reduced pressure, yielding a thick brown oil. The oil was purified by column chromatography (silica gel, eluent EtOAc and Et_3N (100:1)) to give **15** as a light brown oil, which crystallized on standing. Yield: 4.31 g (69%). Light brown single crystals suitable for X-ray diffraction were obtained from a saturated diethyl ether solution at 4 °C. ^1H NMR ($CDCl_3$, 299.9 MHz): δ 7.78 (4H, d, ^3J = 9.0 Hz, 2-$C_6\underline{H}_4Me$), 7.33 (4H, d, ^3J = 9.0 Hz, 3-$C_6\underline{H}_4Me$), 7.20−7.00 (5H, m, $\underline{Ph}$), 5.43 (2H, app. t, ^3J = 6.2 Hz, $N\underline{H}$), 3.46 (2H, s, $C\underline{H}_2Ph$), 2.94 (4H, app. q, ^3J = 6.2 Hz, $C\underline{H}_2NHS$), 2.54 (4H, t, ^3J = 3.8 Hz, $C\underline{H}_2CH_2NHS$), 2.45 (6H, s, $C_6H_4\underline{Me}$). $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz): δ 143.3 (1-C_6H_4), 137.7 ($\underline{4\text{-}C}_6H_4$), 136.6 (1-$C_6H_5$), 129.7 (2-$C_6H_4$), 128.9 (2-$C_6H_5$), 128.5 (3-$C_6H_5$), 127.1 (3-$C_6H_4$), 58.4 ($\underline{C}H_2Ph$), 53.1 ($\underline{C}H_2NHS$), 40.6 ($\underline{C}H_2NHS$), 21.5 ($C_6H_4\underline{Me}$). ES-MS: $[M + H]^+$ 502.1834 (calcd for $C_{25}H_{32}N_3O_4S_2$, 502.1834). IR (NaCl plates, Nujol mull, cm^{-1}): 3283 (m), 1924 (w), 1812 (w), 1494 (s), 1261 (s), 1093 (s), 1028 (s), 1020 (m) 997 (m), 847 (w), 769 (w). Anal. Found (calcd for $C_{25}H_{31}N_3O_4S_2$): C, 59.41 (59.85); H, 6.22 (6.23); N, 8.04 (8.38).

$H_2N_2^{Ms}N^{Ph}$ (16). To a solution of 1-(methylsulfonyl)aziridine (2.77 g, 0.022 mol) in EtOH (100 mL) was added benzylamine (1.14 mL, 0.010 mol) dropwise. After stirring at 40 °C for 16 h the resulting yellow solution was concentrated under reduced pressure and purified using column chromatography (eluent ethyl acetate/pentane/NH_4OH, 50:10:1) to give **16** as a light yellow powder. Yield: 3.30 g (95%). Diffraction-quality crystals were grown from a concentrated benzene solution. ^1H NMR ($CDCl_3$, 299.9 MHz): δ 7.25−7.00 (5H, m, Ph), 5.20 (2H, br t, ^3J = 5.54 Hz, NH), 3.56 (2H, s, $C\underline{H}_2Ph$), 3.10 (4H, q, ^3J = 5.49 Hz, ^4J = 4.93 Hz, $C\underline{H}_2NHS$), 2.84 (6H, s, $SO_2\underline{Me}$), 2.62 (4H, t, ^3J = 5.21 Hz, $C\underline{H}_2CH_2NHS$). $^{13}C\{^1H\}$ ($CDCl_3$, 75.4 MHz): δ 138.1 (*i*-C_6H_5), 129.9 (*o*-C_6H_5), 129.2 (*m*-C_6H_5), 128.2 (*p*-C_6H_5), 59.1 ($\underline{C}H_2Ph$), 53.7 ($\underline{C}H_2NH$), 40.9 ($\underline{C}H_2CH_2NH$), 39.4 ($S\underline{Me}$). ES-MS: $[M + 1]^+$ 350.1195 (calcd for $C_{13}H_{24}N_3O_4S_2$, 350.1208). IR (NaCl plates, Nujol mull, cm^{-1}): 3277 (m), 1496 (s), 1466 (s), 1378 (s), 1332 (s), 1279 (w), 1233 (w), 1161 (s), 1136 (m), 1089 (m), 1048 (w), 993 (m), 978 (m), 940 (vw), 926 (w), 907 (w), 820 (m), 783 (s), 750 (s), 731 (m), 700 (m), 668 (w), 615 (w), 600 (w), 524 (w). Anal. Found (calcd for $C_{13}H_{23}N_3O_4S_2$): C, 44.18 (44.68); H, 6.68 (6.63); N, 11.30 (12.02).

$Al(CyN_2^{Ts})Et(THF)$ (17). To a solution of $H_2CyN_2^{Ts}$ (2.00 g, 4.73 mmol) in THF (30 mL) cooled to 0 °C was added dropwise a solution of $AlEt_3$ in hexanes (1.0 M, 5.68 mL, 5.68 mmol). The mixture was allowed to warm to room temperature and stirred for 16 h. The orange solution was concentrated to half its volume under reduced pressure, and hexanes (30 mL) was added. The resulting white solid was filtered, washed with hexanes (3 × 15 mL), and dried *in vacuo*, giving **17** as a white solid. Yield: 1.80 g (70%). Diffraction-quality crystals were grown from a saturated solution of THF and hexanes at room temperature. ^1H NMR (C_6D_6, 299.9 MHz, 303 K): δ 7.94 (4H, d, ^3J = 8.1 Hz, 2-$C_6\underline{H}_4Me$), 6.84 (4H, d, ^3J = 8.1 Hz, 3-$C_6\underline{H}_4Me$), 3.56 (4H, m, $\underline{THF}$), 3.34 (2H, d, ^3J = 8.7 Hz, 1,6-$C_6\underline{H}_{10}N_2$), 2.36 (2H, m, $C_6\underline{H}_{10}N_2$), 1.92 (6H, s, $C_6H_4\underline{Me}$), 1.78 (3H, t, ^3J = 8.1 Hz, $AlCH_2\underline{Me}$), 1.42 (4H, m, THF), 1.15 (6H, br m, overlapping $C_6\underline{H}_{10}N_2$, $C\underline{H}_2Me$, and $C_6\underline{H}_{10}N_2$), 0.82 (2H, br m, $C_6\underline{H}_{10}N_2$) ppm. A satisfactory ^{13}C NMR spectrum could not be obtained due to the insolubility and fluxional nature of the compound. IR (NaCl plates, Nujol mull, cm^{-1}): 1597 (w), 1495 (w), 1209 (w), 1147 (m), 1108 (m), 1088 (m), 1050 (m), 1021 (w), 983 (m), 958 (m), 903 (m), 865 (m), 842 (m), 824 (m), 816 (w), 798 (w), 733 (m), 720 (w), 678 (m), 670 (m), 615 (m), 583 (m), 553 (s). Anal. Found (calcd for $C_{26}H_{37}AlN_2O_5S_2$): C, 56.82 (56.91); H, 6.84 (6.80); N, 5.07 (5.11).

$Al(CyN_2^{SO_2Mes})Et(THF)$ (18). To a solution of $H_2CyN_2^{SO_2}Mes$ (1.0 g, 2.04 mmol) in THF (10 mL) was added a solution of $AlEt_3$ in hexanes (1.0 M, 2.24 mL, 2.24 mmol). The mixture was heated up to 80 °C for 16 h. The volatiles of the resulting orange solution were removed under reduced pressure, and the white solid was dissolved in a minimum volume of THF and layered with hexanes (40 mL). The resulting white solid was filtered, washed with hexanes (3 × 15 mL), and dried *in vacuo*, giving **18** as a white solid. Yield: 0.81 g (66%). ^1H NMR (C_6D_6, 299.9 MHz, 303 K): δ 6.67 (4H, s, $C_6\underline{H}_2Me_3$), 3.54 (4H, m, THF), 3.40 (2H, br s, 1,6-$C_6\underline{H}_{10}N_2$), 2.70 (12H, br s, 2,6-$NC_6H_2\underline{Me}_3$), 1.94 (6H, s, 4-$NC_6H_2\underline{Me}_3$), 1.94 (2H, m, $C_6\underline{H}_{10}N_2$), 1.71 (3H, t, ^3J = 8.1 Hz, $CH_2\underline{Me}$), 1.42 (4H, m, THF), 1.07 (4H, br m, overlapping $C_6\underline{H}_{10}N_2$ and $C\underline{H}_2Me$), 0.97 (4H, br m, $C_6\underline{H}_{10}N_2$) ppm. A satisfactory ^{13}C NMR spectrum could not be obtained due to the fluxional nature of the compound. IR (NaCl plates, Nujol mull, cm^{-1}): 1602 (w), 1565 (w), 1402 (w), 1292 (m), 1253 (m), 1211 (w), 1132 (m), 1115 (m), 1098 (m), 1074 (m), 1054 (m), 982 (m), 932 (w), 898 (m), 865 (w), 847 (w), 833 (m), 796 (w), 732 (w), 703 (m), 689 (m), 674 (m), 660 (m), 619 (m), 591 (m). Anal. Found (calcd for $C_{30}H_{45}AlN_2O_5S_2$): C, 59.69 (59.58); H, 7.39 (7.50); N, 4.69 (4.63). ES-MS: *m*/*z* 503 $[M - Et, THF + H]^+$ 25%.

$Al(N_2^{Ts}N^{Ph})Et$ (19). $AlEt_3$ (2.2 mL, 1 M in hexanes) was added to a solution of a solution of $H_2N_2^{Ts}N^{Ph}$ (1.00 g, 2.0 mmol) in THF (30 mL) at 0 °C. The mixture was stirred at RT for 4 h, resulting in a colorless solution. Removal of the volatiles under reduced pressure yielded **19** as a white solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.70 g (63%). Diffraction-quality crystals were grown from a concentrated dichloromethane solution layered with hexanes. ^1H NMR (CD_2Cl_2, 299.9 MHz): δ 7.83 (4H, d, ^3J = 8.0 Hz, 2-$C_6\underline{H}_4Me$), 7.41 (3H, m, overlapping 3- and 4-C_6H_5), 7.28 (4H, d, ^3J = 8.0 Hz, 3-$C_6\underline{H}_4Me$), 7.41 (2H, m, 2-C_6H_5), 3.97 (2H, s, $C\underline{H}_2C_6H_5$), 3.23 (2H, m, $TsNC\underline{H}_2CH_2$), 3.00 (2H, m, $TsNC\underline{H}_2CH_2$), 2.83 (2H, m, $TsNCH_2C\underline{H}_2$), 2.62 (2H, m, $TsNCH_2C\underline{H}_2$), 2.42 (6H, s, $C_6H_4\underline{Me}$), 1.26 (3H, t, ^3J = 8.0 Hz, $AlCH_2\underline{Me}$), 0.42 (2H, q, ^3J = 8.0 Hz, $AlC\underline{H}_2Me$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 142.7 (1-C_6H_4Me), 137.6 (4-C_6H_4Me), 131.3 (4-C_6H_5), 129.7 (1-C_6H_5), 129.4 (3-C_6H_4Me), 129.3 (2-C_6H_5), 128.3 (3- C_6H_5), 127.3 (2-C_6H_4Me), 55.0 ($N\underline{C}H_2C_6H_5$), 48.9 ($TsNCH_2\underline{C}H_2$), 39.7 ($TsN\underline{C}H_2CH_2$), 21.2 ($C_6H_4\underline{Me}$), 8.7 ($AlCH_2\underline{Me}$), −1.5 ($Al\underline{C}H_2Me$). IR (NaCl plates, Nujol mull, cm^{-1}): 3066 (w), 1495 (w), 1310 (s), 1303 (s), 1286 (w), 1267 (w), 1244 (w), 1152 (s), 1126 (m), 1097 (m), 1053 (w), 1043 (w), 1022 (w), 998 (m), 970 (w), 940 (w), 889 (w), 845 (w), 815 (w), 799 (w), 742 (w), 711 (w), 702 (w), 683 (w), 652 (w),630 (w). Anal. Found (calcd for $C_{27}H_{34}AlN_3O_4S_2$): C, 58.30 (58.36); H, 6.28 (6.17); N, 7.56 (7.46).

$Al(N_2^{Ts}N^{OMe})Et$ (20). $AlEt_3$ (2.34 mL, 1 M in hexanes) was added to a solution of $H_2N_2^{Ts}N^{OMe}$ (1.00 g, 2.13 mmol) in THF (30 mL) at 0 °C. The mixture was stirred at RT for 3 h, resulting in a colorless solution. Removal of the volatiles under reduced pressure yielded a white solid, which was recrystallized from a

---

(102) Herbert, B. *Jus. Liebigs. Ann. Chem.* **1950**, *566*, 210–244.

concentrated toluene solution at 100 °C to yield **20** as a white solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.60 g (54%). Diffraction-quality crystals were grown from a concentrated dichloromethane solution layered with hexanes. ^{1}H NMR (CD_2Cl_2, 299.9 MHz): δ 7.78 (4H, d, ^3J = 6.0 Hz, 2-C_6H_4Me), 7.26 (4H, d, ^3J = 6.0 Hz, 3-C_6H_4Me), 3.57 (6H, app. t, ^3J = 6.0 Hz, OCH_2CH_2), 3.25 (3H, s, OMe), 3.01−2.92 (10H, m, overlapping CH_2), 2.40 (6H, s, C_6H_4Me), 1.15 (3H, t, ^3J = 9.0 Hz, $AlCH_2Me$), 0.28 (2H, q, ^3J = 9.0 Hz, $AlCH_2Me$) ppm . $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 142.9 (1-C_6H_4Me), 138.0 (4-C_6H_4Me), 129.6 (3-C_6H_4Me), 127.6 (2-C_6H_4Me), 67.4 (MeO), 58.7 (OCH_2CH_2), 51.7 ($TsNCH_2CH_2$), 51.0 ($TsNCH_2CH_2$), 40.3 (OCH_2CH_2), 21.5 (C_6H_4Me), 8.9 ($AlCH_2Me$), −2.1 ($AlCH_2Me$). IR (NaCl plates, Nujol mull, cm^{-1}): 1598 (w), 1350 (w), 1304 (s), 1285 (m), 1245 (m), 1227 (w), 1203 (w), 1146 (s), 1095 (s), 1067 (w), 1035 (m), 1023 (w), 991 (s), 931 (w), 912 (w), 899 (w), 846 (m), 818 (m), 800 (w), 748 (w), 728 (w), 712 (w), 679 (m), 652 (w), 630 (w), 618 (w). Anal. Found (calcd for $C_{23}H_{34}AlN_3O_5S_2$): C, 52.59 (52.75); H, 6.40 (6.54); N, 7.86 (8.02).

Al($N_2{}^{Ts}N^{py}$)Et (21). $AlEt_3$ (2.2 mL, 1 M in hexanes) was added to a solution of $H_2N_2{}^{Ts}N^{py}$ (1.00 g, 2.00 mmol) in THF (30 mL) at 0 °C. The mixture was stirred at RT for 16 h, resulting in a colorless solution with a white precipitate. Removal of the volatiles under reduced pressure yielded a white solid, which was recrystallized from a concentrated THF and dichloromethane (1:1) solution to yield **21** as a white solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.69 g (63%). Diffraction-quality crystals were grown from a concentrated dichloromethane solution layered with hexanes. ^{1}H NMR (CD_2Cl_2, 299.9 MHz): δ 9.05 (1H, dd, ^3J = 7.6 Hz, ^4J = 1.5 Hz, 2-NC_5H_4), 8.04 (1H, dt, ^3J = 7.6 Hz, ^3J = 7.0 Hz, 3-NC_5H_4), 7.71 (4H, d, ^3J = 8.2 Hz, 2-C_6H_4Me), 7.63 (1H, dd, ^3J = 7.0 Hz, ^3J = 7.6 Hz, 4-NC_5H_4), 7.43 (1H, d, ^3J = 7.0 Hz, 5-NC_5H_4), 7.19 (4H, d, ^3J = 8.2 Hz, 3-C_6H_4Me), 4.06 (2H, s, $pyCH_2N$), 3.09 (4H, m, overlapping $TsNCH_2CH_2N$), 2.75−2.45 (4H, m, $TsNCH_2CH_2N$), 2.37 (6H, s, C_6H_4Me), 0.91 (3H, t, ^3J = 7.6 Hz, $AlCH_2Me$), 0.65 (2H, q, ^3J = 7.6 Hz, $AlCH_2Me$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 154.5 (6-NC_5H_4), 150.1 (1-C_6H_4Me), 142.0 (2-NC_5H_4), 140.9 (4-C_6H_4Me), 140 (3-NC_5H_4), 129.5 (3-C_6H_4Me), 127.5 (2-C_6H_4Me), 125.5 (4-NC_5H_4), 124.1 (5-NC_5H_4), 68.3 ($pyCH_2N$), 57.11 ($TsNCH_2CH_2N$), 42.4 ($TsNCH_2CH_2N$), 26.1 ($AlCH_2Me$), 21.6 (C_6H_4Me), 10.1 ($AlCH_2Me$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1653 (w), 1306 (m), 1281 (m), 1281 (m), 1261 (m), 1162 (w), 1141 (m), 1095 (w), 1022 (w), 980 (m), 957 (w), 813 (w), 799 (w), 723 (w), 672 (w). Anal. Found (calcd for $C_{26}H_{33}AlN_4O_4S_2$): C, 55.98 (56.10); H, 5.86 (5.98); N, 9.98 (10.06).

Al($N_2{}^{Ts}N^{py}$)(O^iPr) (22). A solution of $Al(O^iPr)Et_2$ (0.29 g, 2.0 mmol), $H_2N_2{}^{Ts}N^{py}$ (1.0 g, 2.00 mmol), and toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded a brown solid, which was washed with Et_2O (3 × 20 mL) and dried *in vacuo*. Yield: 0.77 g (66%). ^{1}H NMR (CD_2Cl_2, 499.9 MHz): δ 9.73 (1H, d, ^3J = 6.3 Hz, 2-NC_5H_4), 8.04 (1H, dt, ^3J = 7.8 Hz, ^4J = 1.5 Hz, 4-NC_5H_4), 7.78 (4H, d, ^3J = 7.8 Hz, 2-C_6H_4Me), 7.63 (1H, t, ^3J = 6.3 Hz, 3-NC_5H_4), 7.41 (1H, d, ^3J = 7.8 Hz, 5-NC_5H_4), 7.20 (4H, d, ^3J = 7.8 Hz, 3-C_6H_4Me), 4.50 (1H, sept., ^3J = 6.0 Hz, $CHMe_2$), 4.06 (2H, s, $pyCH_2N$), 3.16 (2H, m, $TsNCH_2CH_2N$), 3.08 (2H, m, $TsNCH_2CH_2N$), 2.79 (2H, m, $TsNCH_2CH_2N$), 2.60 (2H, m, $TsNCH_2CH_2N$), 2.37 (6H, s, C_6H_4Me), 1.13 (6H, d, ^3J = 6.0 Hz, $CHMe_2$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 155.4 (6-NC_5H_4), 152.1(2-NC_5H_4), 142.4 (4-NC_5H_4), 141.7 (1-C_6H_4Me), 141.1 (4-C_6H_4Me), 129.2 (3-C_6H_4Me), 127.2 (2-C_6H_4Me), 124.8 (3-NC_5H_4), 123.5 (5-NC_5H_4), 63.8 ($CHMe_2$) 57.1 ($pyCH_2N$), 54.6 ($TsNCH_2CH_2N$), 42.6 ($TsNCH_2CH_2N$), 27.6 ($CHMe_2$), 21.4 (C_6H_4Me) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3050 (w), 1734 (w), 1559 (w), 1298 (s), 1144 (m), 1093 (m), 1025 (w), 971 (w), 816 (w), 722 (w), 668 (w). Anal. Found (calcd for $C_{27}H_{35}AlN_4O_5S_2$): C, 55.10 (55.27); H, 6.05 (6.01); N, 9.60 (9.55).

Al($N_2{}^{Ts}N^{py}$)(OBn) (23). A solution of $Al(OBn)Et_2$ (0.19 g, 1.0 mmol) and $H_2N_2{}^{Ts}N^{py}$ (0.5 g, 1.00 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded a brown solid, which was recrystallized from a concentrated THF and pentane (1:1) solution to yield **23** as a white solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.38 g (61%). ^{1}H NMR (CD_2Cl_2, 499.9 MHz): δ 9.35 (1H, d, ^3J = 4.5 Hz, 2-NC_5H_4), 7.96 (1H, dt, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 4-NC_5H_4), 7.80 (4H, d, ^3J = 8.1 Hz, 2-C_6H_4Me), 7.39 (4H, d, ^3J = 7.5 Hz, overlapping 2-C_6H_5, 3-NC_5H_4 and 5-NC_5H_4), 7.28 (2H, t, ^3J = 7.5 Hz, 3-C_6H_5) 7.15 (5H, d, ^3J = 8.1 Hz, overlapping 3-C_6H_4Me and 4-C_6H_5), 5.18 (2H, s, $OCH_2C_6H_5$), 4.00 (2H, s, $pyCH_2N$), 3.25 (2H, m, $TsNCH_2CH_2N$), 3.12 (2H, m, $TsNCH_2CH_2N$), 2.86 (2H, m, $TsNCH_2CH_2N$), 2.61 (2H, m, $TsNCH_2CH_2N$), 2.36 (6H, s, C_6H_4Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 155.1 (6-NC_5H_4), 152.1 (2-NC_5H_4), 147.0 (1-C_6H_5), 142.7 (4-NC_5H_4), 141.7 (1-C_6H_4Me), 141.0 (4-C_6H_4Me), 129.2 (3-C_6H_4Me), 128.0 (3-C_6H_5), 127.4 (2-C_6H_5), 127.0 (2-C_6H_4Me), 125.8 (4-C_6H_5), 124.9 (3- NC_5H_4), 123.9 (5-C_6H_5), 66.2 ($OCH_2C_6H_5$), 55.8 ($pyCH_2N$), 52.7 ($TsNCH_2CH_2N$), 42.4 ($TsNCH_2CH_2N$), 21.4 (C_6H_4Me) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1559 (w), 1334 (m), 1261 (s), 1183 (m), 1104 (s), 1012 (s), 801 (m), 722 (m), 689 (w). Anal. Found (calcd for $C_{31}H_{35}AlN_4O_5S_2$): C, 58.75 (58.66); H, 5.61 (5.56); N, 8.81 (8.83).

[Al($N_2{}^{Ts}N^{O}$)]$_2$ (25). A mixture of $Al(O^iPr)Et_2$ (0.31 g, 2.13 mmol) and $H_2N_2{}^{Ts}N^{OMe}$ (1.00 g, 2.13 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded crude Al($N_2{}^{Ts}N^{OMe}$)(O^iPr) a light yellow solid. This was heated at 150 °C for 48 h under a dynamic vacuum (1 mbar). The resulting white solid (**25**) was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.75 g (73%). Diffraction-quality crystals were grown from a saturated solution of dichloromethane at room temperature. ^{1}H NMR (CD_2Cl_2, 499.9 MHz): δ 7.91 (4H, d, ^3J = 8.2 Hz, 2-C_6H_4Me), 7.37 (4H, d, ^3J = 8.2 Hz, 3-C_6H_4Me), 4.14 (2H, t, ^3J = 5.7 Hz, OCH_2), 3.29 (2H, m, $TsNCH_2CH_2N$), 3.15 (2H, m, $TsNCH_2CH_2N$), 2.83 (2H, t, ^3J = 5.7 Hz, OCH_2CH_2), 2.66 (2H, m, $TsNCH_2CH_2N$), 2.62 (2H, m, $TsNCH_2CH_2N$), 2.42 (6H, s, C_6H_4Me) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.4 MHz): δ 142.7 (1-C_6H_4Me), 140.5 (4-C_6H_4Me), 130.2 (3-C_6H_4Me), 127.4 (2-C_6H_4Me), 60.2 (OCH_2), 53.6 ($TsNCH_2CH_2N$), 52.9 (OCH_2CH_2), 42.2 ($TsNCH_2CH_2N$), 21.8 (C_6H_4Me) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3029 (w), 1559 (w), 1281 (s), 1158 (w), 1140 (m), 1104 (m), 1066 (w), 1048 (w), 1034 (w), 967 (m), 911 (w), 869 (w), 829 (m), 742 (m), 722 (m), 694 (w), 667 (w). Anal. Found (calcd for $C_{40}H_{52}Al_2N_6O_{10}S_4$): C, 50.14 (50.09); H, 5.56 (5.46); N, 8.88 (8.76).

Al($N_2{}^{Tm}N^{Ph}$)(O^iPr) (26). A mixture of $Al(O^iPr)Et_2$ (0.12 g, 0.86 mmol) and $H_2N_2{}^{Tm}N^{Ph}$ (0.30 g, 0.86 mmol) in toluene (30 mL) was heated at 100 °C for 48 h, resulting in a colorless solution with a white precipitate. This was filtered and washed with pentane (3 × 20 mL) and dried *in vacuo* to give **26** as a light brown solid. Yield: 0.19 g (51%). ^{1}H NMR (CD_2Cl_2 + NC_5D_5, 299.9 MHz): δ 7.20−7.05 (5H, m, overlapping NCH_2(2-C_6H_5), NCH_2(3-C_6H_5), and NCH_2(4-C_6H_5)), 4.31 (1H, sept., ^3J = 6 Hz, $OCHMe_2$), 4.16 (2H, s, $NCH_2C_6H_5$), 3.43 (2H, m, $TsNCH_2CH_2N$), 3.26 (2H, m, $TsNCH_2CH_2N$), 2.95 (2H, m, $TsNCH_2CH_2N$), 2.68 (2H, m, $TsNCH_2CH_2N$), 2.57 (6H, s, SO_2Me), 1.28 (6H, d, ^3J = 6 Hz, $OCHMe_2$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2 + NC_5D_5, 75.4 MHz): δ 131.8 (1-C_6H_5), 131.5 (3-C_6H_5), 128.6 (2-C_6H_5), 128.5 (4-C_6H_5), 63.8 ($OCHMe_2$), 57.4 ($NCH_2C_6H_5$), 50.9 ($MsNCH_2CH_2N$), 42.4 ($MsNCH_2CH_2N$), 39.6 (SO_2Me), 27.6 ($OCHMe_2$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1496 (w), 1328 (w), 1291 (s), 1264 (s), 1230 (w), 1180 (m), 1120 (s), 1104 (m), 1079 (w), 1064 (w), 1019 (s), 982 (m), 898 (w), 776 (m), 738 (m), 706 (m), 669 (w), 652 (w). Anal. Found (calcd for $C_{16}H_{28}AlN_3O_5S_2$): C, 44.36 (44.33); H, 6.46 (6.51); N, 9.69 (9.66).

Al($\mathbf{N_2}^{\mathbf{Tm}}\mathbf{N}^{\mathbf{Ph}}$)(OBn) (27). A mixture of Al(OBn)$\mathrm{Et_2}$ (0.17 g, 0.86 mmol) and $\mathrm{H_2N_2}^{\mathrm{Tm}}\mathrm{N}^{\mathrm{Ph}}$ (0.30 g, 0.86 mmol) in toluene (30 mL) was heated at 100 °C for 48 h, resulting in a colorless solution with a white precipitate. This was then filtered and washed with pentane (3 × 20 mL) and dried *in vacuo* to give **27** as a cream solid. Yield: 0.27 g (65%). ^{1}H NMR ($\mathrm{CD_2Cl_2 + NC_5D_5}$, 299.9 MHz): δ 7.53 (2H, d, ^3J = 8.3 Hz, $\mathrm{OCH_2(2\text{-}C_6H_5)}$), 7.20−7.08 (8H, m, overlapping $\mathrm{OCH_2(3\text{-}C_6H_5)}$, $\mathrm{OCH_2(4\text{-}C_6H_5)}$, $\mathrm{NCH_2(2\text{-}C_6H_5)}$, $\mathrm{NCH_2(3\text{-}C_6H_5)}$, and $\mathrm{NCH_2(4\text{-}C_6H_5)}$), 5.11 (2H, s, $\mathrm{OC\underline{H}_2C_6H_5}$), 3.97 (2H, s, $\mathrm{NC\underline{H}_2C_6H_5}$), 3.57 (2H, m, $\mathrm{TsNC\underline{H}_2C\underline{H}_2N}$), 3.31 (2H, m, $\mathrm{TsNC\underline{H}_2CH_2N}$), 2.95 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.71 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.59 (6H, s, $\mathrm{SO_2Me}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2 + NC_5D_5}$, 75.4 MHz): δ 145.5 ($\mathrm{OCH_2(1\text{-}C_6H_5)}$), 132.9 ($\mathrm{NCH_2(1\text{-}C_6H_5)}$), 131.5 ($\mathrm{OCH_2(2\text{-}C_6H_5)}$), 128.9 ($\mathrm{NCH_2(6\text{-}C_6H_5)}$), 128.8 ($\mathrm{OCH_2(3\text{-}C_6H_5)}$), 128.6 ($\mathrm{NCH_2(3\text{-}C_6H_5)}$), 126.9 ($\mathrm{OCH_2(4\text{-}C_6H_5)}$), 126.5 ($\mathrm{NCH_2(4\text{-}C_6H_5)}$), 65.6 ($\mathrm{O\underline{C}H_2C_6H_5}$), 56.9 ($\mathrm{N\underline{C}H_2C_6H_5}$), 50.8 ($\mathrm{SO_2Me}$), 42.7 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 39.9 ($\mathrm{TsN\underline{C}H_2CH_2N}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3039 (w), 1296 (s), 1273 (m), 1226 (w), 1166 (m), 1149 (w), 1133 (m), 1098 (m), 1080 (w), 1024 (m), 983 (m), 800 (w), 772 (m), 742 (w), 704 (w), 668 (w), 656 (w). Anal. Found (calcd for $\mathrm{C_{20}H_{28}AlN_3O_5S_2}$): C, 49.92 (49.88); H, 5.85 (5.86); N, 8.70 (8.73).

[Al($\mathbf{N_2}^{\mathbf{Ts}}\mathbf{N}^{\mathbf{Ph}}$)Cl]$_2$ (28). $\mathrm{AlMe_2Cl}$ (2.0 mL, 1 M in hexanes) was added dropwise to a solution of $\mathrm{H_2N_2}^{\mathrm{Ts}}\mathrm{N}^{\mathrm{ph}}$ (1.00 g, 2.00 mmol) in $\mathrm{C_6H_6}$ (30 mL). The mixture was stirred at RT for 16 h, resulting in a yellow solution. Removal of the volatiles under reduced pressure yielded a light yellow solid, which was washed with ether (3 × 15 mL) and recrystallized from a concentrated dichloromethane solution (10 mL) layered with hexanes (30 mL) to yield **28** as a light yellow solid. This was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.65 g (58%). Diffraction-quality crystals were grown from a saturated solution of dichloromethane layered with hexanes at room temperature. ^{1}H NMR ($\mathrm{C_6D_6}$, 299.9 MHz): δ 8.72 (2H, d, ^3J = 8.1 Hz, bridging $\mathrm{2\text{-}C_6\underline{H}_4Me}$), 8.31 (2H, d, ^3J = 8.7 Hz, terminal $\mathrm{2\text{-}C_6\underline{H}_4Me}$), 7.18 (2H, d, ^3J = 8.1 Hz, bridging $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 7.00 (1H, m, $\mathrm{4\text{-}C_6H_5}$), 6.90 (2H, t, ^3J = 7.5 Hz, $\mathrm{3\text{-}C_6H_5}$), 6.78 (2H, d, ^3J = 8.7 Hz, terminal $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 6.90 (2H, d, ^3J = 7.5 Hz, $\mathrm{2\text{-}C_6H_5}$), 4.55 (1H, d, ^2J = 15 Hz, $\mathrm{NC\underline{H}_2C_6H_5}$), 4.44 (1H, d, ^2J = 15 Hz, $\mathrm{NC\underline{H}_2C_6H_5}$), 3.95 (1H, dt, ^2J = 6.9 Hz, ^3J = 4.8 Hz, $\mathrm{TsNC\underline{H}_2CH_2N}$), 3.26 (1H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.95−2.55 (4H, m, $\mathrm{TsNC\underline{H}_2C\underline{H}_2N}$), 1.96 (3H, s, bridging $\mathrm{C_6H_4\underline{Me}}$), 1.83 (5H, s, overlapping $\mathrm{C_6H_4\underline{Me}}$ and $\mathrm{TsNC\underline{H}_2C\underline{H}_2N}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.4 MHz): δ 142.8 ($\mathrm{1\text{-}C_6H_4Me}$), 141.6 ($\mathrm{1\text{-}C_6H_4Me}$), 140.5 ($\mathrm{4\text{-}C_6H_4Me}$), 136.0 ($\mathrm{4\text{-}C_6H_4Me}$), 132.0 ($\mathrm{2\text{-}C_6H_5}$), 131.4 ($\mathrm{1\text{-}C_6H_5}$), 129.4 ($\mathrm{3\text{-}C_6H_4Me}$), 129.1 ($\mathrm{3\text{-}C_6H_4Me}$), 128.7 ($\mathrm{2\text{-}C_6H_4Me}$), 128.6 ($\mathrm{2\text{-}C_6H_4Me}$), 128.5 ($\mathrm{4\text{-}C_6H_5}$), 128.4 ($\mathrm{4\text{-}C_6H_5}$), 55.6 ($\mathrm{NC\underline{H}_2C_6H_5}$) 47.4 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 42.2 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 41.8 (overlapping $\mathrm{TsN\underline{C}H_2\underline{C}H_2N}$), 26.1 ($\mathrm{AlCH_2\underline{Me}}$), 21.6 ($\mathrm{C_6H_4\underline{Me}}$), 10.1 ($\mathrm{Al\underline{C}H_2Me}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 2726 (w), 1506 (w), 1304 (m), 1262 (s), 1155 (m), 1062 (s), 1021 (s), 1003 (w), 807 (w), 722 (s), 668 (w). Anal. Found (calcd for $\mathrm{C_{58}H_{58}Al_2Cl_2N_6O_8S_4}$): C, 53.47 (53.42); H, 5.32 (5.20); N, 7.44 (7.44).

Al($\mathbf{N_2}^{\mathbf{Ts}}\mathbf{N}^{\mathbf{Ph}}$)($\mathbf{OCH_2CH_2NH_2}$) (29). A mixture of Al($\mathrm{OCH_2CH_2NH_2}$)$\mathrm{Et_2}$ (0.14 g, 1.0 mmol) and $\mathrm{H_2N_2}^{\mathrm{Ts}}\mathrm{N}^{\mathrm{Ph}}$ (0.50 g, 1.00 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded **29** as a cream solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.40 g (68%). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 299.9 MHz): δ 7.71 (4H, d, ^3J = 7.8 Hz, $\mathrm{2\text{-}C_6\underline{H}_4Me}$), 7.29 (3H, m, overlapping $\mathrm{2\text{-}C_6H_5}$ and $\mathrm{4\text{-}C_6H_5}$), 7.23 (4H, d, ^3J = 7.8 Hz, $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 7.04 (2H, m, $\mathrm{3\text{-}C_6H_5}$), 4.81 (2H, br t, ^3J = 6.0 Hz, $\mathrm{N\underline{H}_2}$), 3.87 (2H, s, $\mathrm{NC\underline{H}_2C_6H_5}$), 3.87 (2H, t, ^3J = 6.0 Hz, $\mathrm{C\underline{H}_2O}$), 3.20 (2H, m, $\mathrm{TsNC\underline{H}_2CH_2N}$), 3.01 (2H, m, $\mathrm{C\underline{H}_2NH_2}$), 2.73 (2H, m, $\mathrm{TsNC\underline{H}_2CH_2N}$), 2.56 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.38 (6H, s, $\mathrm{C_6H_4\underline{Me}}$), 2.15 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$, 75.4 MHz): δ 142.8 ($\mathrm{1\text{-}C_6H_4Me}$), 138.1 ($\mathrm{4\text{-}C_6H_4Me}$), 131.8 ($\mathrm{2\text{-}C_6H_5}$), 131.7 ($\mathrm{1\text{-}C_6H_5}$), 129.6 ($\mathrm{3\text{-}C_6H_4Me}$), 128.9 ($\mathrm{4\text{-}C_6H_5}$), 128.8 ($\mathrm{3\text{-}C_6H_5}$), 127.4 ($\mathrm{2\text{-}C_6H_4Me}$), 60.6 ($\mathrm{O\underline{C}H_2CH_2NMe_2}$), 55.2 ($\mathrm{N\underline{C}H_2C_6H_5}$), 44.8 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 42.6 ($\mathrm{O\underline{C}H_2}$), 41.7 ($\mathrm{TsN\underline{C}H_2CH_2N}$), 21.5 ($\mathrm{C_6H_4\underline{Me}}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3308 (m), 3262 (w), 1598 (w), 1299 (s), 1260 (s), 1154 (s), 1091 (s), 1020 (m), 974 (m), 908 (w), 851 (w), 803 (w), 722 (m), 668 (w). Anal. Found (calcd for $\mathrm{C_{27}H_{35}AlN_4O_5S_2}$): C, 55.42 (55.27); H, 6.11 (6.01); N, 9.57 (9.55).

Al($\mathbf{N_2}^{\mathbf{Ts}}\mathbf{N}^{\mathbf{OMe}}$)($\mathbf{OCH_2CH_2NH_2}$) (30). A mixture of Al($\mathrm{OCH_2CH_2NH_2}$)$\mathrm{Et_2}$ (0.15 g, 1.00 mmol) and $\mathrm{H_2N_2}^{\mathrm{Ts}}\mathrm{N}^{\mathrm{OMe}}$ (0.50 g, 1.03 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded **30** as a cream solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.45 g (79%). Diffraction-quality crystals were grown from a saturated solution of dichloromethane layered with hexanes at RT. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 499.9 MHz): δ 7.69 (4H, d, ^3J = 8.0 Hz, $\mathrm{2\text{-}C_6\underline{H}_4Me}$), 7.25 (4H, d, ^3J = 8.0 Hz, $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 4.75 (2H, br t, ^3J = 7.5 Hz, $\mathrm{NH_2}$), 3.78 (2H, t, ^3J = 7.5 Hz, $\mathrm{OCH_2}$), 3.43 (2H, t, ^3J = 7.5 Hz, $\mathrm{H_2NC\underline{H}_2}$), 3.16 (3H, s, OMe), 3.05−2.95 (4H, m, $\mathrm{TsNCH_2}$), 2.72 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.43 (2H, m, $\mathrm{TsNCH_2C\underline{H}_2N}$), 2.20 (6H, s, $\mathrm{C_6H_4\underline{Me}}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 75.4 MHz): δ 142.7 ($\mathrm{1\text{-}C_6H_4Me}$), 138.4 ($\mathrm{4\text{-}C_6H_4Me}$), 129.6 ($\mathrm{3\text{-}C_6H_4Me}$), 127.4 ($\mathrm{2\text{-}C_6H_4Me}$), 67.9 ($\mathrm{O\underline{C}H_2CH_2NH_2}$), 60.5 ($\mathrm{MeO\underline{C}H_2}$), 58.7 (OMe), 50.8 ($\mathrm{TsNCH_2\underline{C}H_2}$), 46.2 ($\mathrm{TsN\underline{C}H_2}$), 42.5 ($\mathrm{OCH_2\underline{C}H_2N}$), 41.9 ($\mathrm{MeOCH_2\underline{C}H_2N}$), 21.5 ($\mathrm{C_6H_4\underline{Me}}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3306 (m), 3268 (m), 2688 (w), 1636 (w), 1307 (w), 1296 (w), 1280 (s), 1258 (m), 1193 (w), 1156 (s), 1145 (m), 1087 (s), 1054 (m), 1018 (m), 976 (m), 906 (w), 808 (w), 736 (w), 667 (w). Anal. Found (calcd for $\mathrm{C_{23}H_{35}AlN_4O_6S_2}$): C, 49.77 (49.80); H, 6.36 (6.26); N, 10.02 (10.10).

Al($\mathbf{N_2}^{\mathbf{Ts}}\mathbf{N}^{\mathbf{py}}$)($\mathbf{OCH_2CH_2NH_2}$) (31). A mixture of Al($\mathrm{OCH_2CH_2NH_2}$)$\mathrm{Et_2}$ (0.14 g, 1.0 mmol) and $\mathrm{H_2N_2}^{\mathrm{Ts}}\mathrm{N}^{\mathrm{py}}$ (0.50 g, 1.00 mmol) in toluene (30 mL) was heated at 100 °C for 48 h. Removal of the volatiles under reduced pressure yielded a brown solid, which was recrystallized from a concentrated THF (10 mL) solution layered with pentane (30 mL). The resulting light brown solid (**31**) was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.44 g (75%).

Major isomer **31a**: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 499.9 MHz): δ 8.87 (1H, d, ^3J = 5.1 Hz, $\mathrm{2\text{-}NC_5H_4}$), 7.86 (1H, dt, ^3J = 7.7 Hz, ^4J = 1.3 Hz, $\mathrm{3\text{-}NC_5H_4}$), 7.72 (5H, d, ^3J = 8.2 Hz, overlapping $\mathrm{2\text{-}C_6\underline{H}_4Me}$ and $\mathrm{4\text{-}NC_5H_4}$), 7.45 (1H, d, ^3J = 7.7 Hz, 5- $\mathrm{NC_5H_4}$), 7.20 (4H, d, ^3J = 8.2 Hz, $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 4.98 (2H, br t, ^3J = 5.5 Hz, $\mathrm{NH_2}$), 4.17 (2H, s, $\mathrm{pyC\underline{H}_2N}$), 3.56 (2H, t, ^3J = 5.5 Hz, $\mathrm{OCH_2}$), 3.25−2.75 (10H, m, overlapping $\mathrm{TsNC\underline{H}_2C\underline{H}_2N}$ and $\mathrm{C\underline{H}_2NH_2}$), 2.37 (6H, s, $\mathrm{C_6H_4\underline{Me}}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 75.4 MHz): δ 152.7 ($\mathrm{6\text{-}NC_5H_4}$), 147.6 ($\mathrm{2\text{-}NC_5H_4}$), 141.9 ($\mathrm{1\text{-}C_6H_4Me}$), 140.7 ($\mathrm{4\text{-}NC_5H_4}$), 139.1 ($\mathrm{4\text{-}C_6H_4Me}$), 130.1 ($\mathrm{5\text{-}NC_5H_4}$), 129.6 ($\mathrm{3\text{-}C_6H_4Me}$), 127.7 ($\mathrm{2\text{-}C_6H_4Me}$), 127.1 ($\mathrm{3\text{-}NC_5H_4}$), 61.8 ($\mathrm{py\underline{C}H_2N}$), 59.9 ($\mathrm{\underline{C}H_2O}$) 57.3 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 43.7 ($\mathrm{\underline{C}H_2NH_2}$), 43.2 ($\mathrm{TsN\underline{C}H_2CH_2N}$), 21.6 ($\mathrm{C_6H_4\underline{Me}}$) ppm.

Minor isomer **31b**: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 499.9 MHz): δ 8.52 (1H, d, ^3J = 5.5 Hz, $\mathrm{2\text{-}NC_5H_4}$), 7.98 (1H, dt, ^3J = 7.9 Hz, ^4J = 1.3 Hz, $\mathrm{3\text{-}NC_5H_4}$), 7.59 (1H, d, ^3J = 7.9 Hz, $\mathrm{5\text{-}NC_5H_4}$), 7.28 (4H, d, ^3J = 7.8 Hz, $\mathrm{2\text{-}C_6\underline{H}_4Me}$), 7.23 (1H, d, ^3J = 7.9 Hz, $\mathrm{5\text{-}NC_5H_4}$), 7.13 (4H, d, ^3J = 8.2 Hz, $\mathrm{3\text{-}C_6\underline{H}_4Me}$), 5.14 (2H, br t, ^3J = 5.7 Hz, $\mathrm{NH_2}$), 3.95 (2H, s, $\mathrm{pyC\underline{H}_2N}$), 3.88 (2H, t, ^3J = 5.7 Hz, $\mathrm{OCH_2}$), 3.11 (2H, t, ^3J = 5.7 Hz, $\mathrm{NH_2CH_2}$), 3.25−2.75 (8H, m, overlapping $\mathrm{TsNC\underline{H}_2C\underline{H}_2N}$), 2.29 (6H, s, $\mathrm{C_6H_4\underline{Me}}$) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CD_2Cl_2}$, 75.4 MHz): δ 152.3 ($\mathrm{6\text{-}NC_5H_4}$), 145.3 ($\mathrm{2\text{-}NC_5H_4}$), 141.6 ($\mathrm{1\text{-}C_6H_4Me}$), 140.6 ($\mathrm{4\text{-}NC_5H_4}$), 140.1 ($\mathrm{4\text{-}C_6H_4Me}$), 137.5 ($\mathrm{5\text{-}NC_5H_4}$), 129.5 ($\mathrm{3\text{-}C_6H_4Me}$), 127.5 ($\mathrm{2\text{-}C_6H_4Me}$), 124.2 ($\mathrm{3\text{-}NC_5H_4}$), 59.7 ($\mathrm{\underline{C}H_2O}$), 66.9 ($\mathrm{py\underline{C}H_2N}$), 54.5 ($\mathrm{TsNCH_2\underline{C}H_2N}$), 43.8 ($\mathrm{\underline{C}H_2NH_2}$), 42.4 ($\mathrm{TsN\underline{C}H_2CH_2N}$), 21.4 ($\mathrm{C_6H_4\underline{Me}}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 3318 (w), 3310 (w), 3202 (w), 3159 (w), 1612 (m), 1266 (s), 1134 (s), 1103 (s), 1085 (s), 1029 (m), 996 (m), 974 (m), 933 (w), 879 (w), 801 (w), 725 (w), 672 (w), 662 (w), 626 (w). Anal. Found (calcd for $\mathrm{C_{26}H_{34}AlN_5O_5S_2}$): C, 53.23 (53.14); H, 5.90 (5.83); N, 11.82 (11.92).

$Al(N_2{}^{Ts}N^{Ph})(OCH_2CH_2NMe_2)$ (32). A mixture of $Al(OCH_2CH_2NMe_2)Et_2$ (0.17 g, 1.0 mmol) and $H_2N_2{}^{Ts}N^{py}$ (0.50 g, 1.00 mmol) in toluene (30 mL) was heated at 100 °C for 16 h. Removal of the volatiles under reduced pressure yielded a cream solid. Recrystallization from a concentrated dichloromethane solution layered with pentane (30 mL) gave **32** as a cream solid, which was washed with pentane (3 × 20 mL) and dried *in vacuo*. Yield: 0.52 g (85%). ^1H NMR (C_6D_6, 299.9 MHz): δ 8.10 (4H, d, ^3J = 8.1 Hz, 2-$C_6\underline{H_4}Me$), 7.03 (3H, m, overlapping 3-C_6H_5 and 4-C_6H_5), 7.15 (4H, d, ^3J = 8.1 Hz, 3-$C_6\underline{H_4}Me$), 6.83 (2H, dd, ^3J = 7.8 Hz, ^4J = 2.1 Hz, 2-C_6H_5), 4.08 (2H, s, $NC\underline{H_2}C_6H_5$), 3.77 (2H, t, ^3J = 6.0 Hz, $OC\underline{H_2}$), 3.15−3.10 (4H, m, $TsNC\underline{H_2}CH_2N$), 2.98 (2H, br t, ^3J = 6 Hz, $OCH_2C\underline{H_2}NMe_2$), 2.69 (6H, s, $OCH_2CH_2N\underline{Me_2}$), 2.65 (4H, m, $TsNCH_2C\underline{H_2}N$), 1.92 (6H, s, $C_6H_4\underline{Me}$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 141.5 (1-C_6H_4Me), 140.9 (4-C_6H_4Me), 134.3 (1-C_6H_5), 131.8 (2-C_6H_5), 129.5 (3-C_6H_4Me), 128.5 (3-C_6H_5), 128.4 (4-C_6H_5), 127.5 (2-C_6H_4Me), 62.6 ($OCH_2\underline{C}H_2NMe_2$), 58.8 ($N\underline{C}H_2C_6H_5$), 57.8 ($O\underline{C}H_2$), 51.3 ($TsNCH_2\underline{C}H_2N$), 46.3 ($OCH_2CH_2N\underline{Me_2}$), 43.0 ($TsN\underline{C}H_2CH_2N$), 21.0 ($C_6H_4\underline{Me}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 2730 (w), 1700 (w), 1301 (m), 1261 (m), 1143 (m), 1092 (s), 1019 (s), 800 (s), 723 (s), 667 (s). Anal. Found (calcd for $C_{29}H_{39}AlN_4O_5S_2$): C, 56.62 (56.66); H, 6.39 (6.39); N, 9.10 (9.11).

$Al(CyN_2{}^{Ts})(OCH_2CH_2NMe_2)$ (33). A mixture of $H_2CyN_2{}^{Ts}$ (1.00 g, 2.37 mmol) and $Al(OCH_2CH_2NMe_2)Et_2$ (0.450 g, 2.60 mmol) in toluene (30 mL) was heated to 100 °C and stirred at this temperature for 16 h. The volatiles were removed under reduced pressure to give white solid. The solid was redissolved in minimal volume of dichloromethane and layered 4-fold with hexanes to give needle-like crystals. The crystals was filtered, washed with hexanes (3 × 15 mL), and dried under vacuum to give **33** as a white solid. Yield: 0.99 g (78%). Diffraction-quality crystals were grown from a saturated solution of dichloromethane and hexanes at room temperature. ^1H NMR (CD_2Cl_2, 299.9 MHz, 303 K): δ 7.78 (4H, d, ^3J = 8.1 Hz, 2-$C_6\underline{H_4}Me$), 7.73 (4H, d, ^3J = 8.1 Hz, 2-$C_6\underline{H_4}Me$), 7.24 (4H, d, ^3J = 8.1 Hz, 3-$C_6\underline{H_4}Me$), 6.84 (4H, d, ^3J = 8.1 Hz, 3-$C_6\underline{H_4}Me$), 4.91 (2H, m, $C_6\underline{H_{10}}N_2$), 4.30 (2H, m, $C_6\underline{H_{10}}N_2$), 4.00 (2H, t, ^3J = 8.4 Hz, $OC\underline{H_2}CH_2NMe_2$), 3.19 (2H, m, $OCH_2C\underline{H_2}NMe_2$), 3.00 (3H, s, $OCH_2CH_2NMe_2$), 2.74 (3H, s, $OCH_2CH_2NMe_2$), 2.59 (2H, m, $C_6\underline{H_{10}}N_2$), 2.38 (3H, s, $C_6H_4\underline{Me}$), 2.14 (3H, s, $C_6H_4\underline{Me}$), 1.40 (2H, m, $C_6\underline{H_{10}}N_2$), 1.00 (4H, m, $C_6\underline{H_{10}}N_2$), 0.84 (2H, m, $C_6\underline{H_{10}}N_2$) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 75.4 MHz): δ 144.2 (4-$\underline{C_6}H_4Me$), 142.9 (4-$\underline{C_6}H_4Me$), 141.8 (1-$\underline{C_6}H_4Me$), 141.1 (1-$\underline{C_6}H_4Me$), 129.3 (3-$\underline{C_6}H_4Me$), 128.4 (3-$\underline{C_6}H_4Me$), 127.4 (2-$\underline{C_6}H_4Me$), 126.1 (2-$\underline{C_6}H_4Me$), 62.3 ($\underline{C_6}H_{10}N_2$), 61.9 ($OCH_2\underline{C}H_2NMe_2$), 58.6 ($\underline{C_6}H_{10}N_2$), 55.7 ($O\underline{C}H_2CH_2NMe_2$), 47.3 ($OCH_2CH_2NMe_2$), 47.0 ($OCH_2CH_2NMe_2$), 32.1 ($\underline{C_6}H_{10}N_2$), 31.9 ($\underline{C_6}H_{10}N_2$), 25.2 ($\underline{C_6}H_{10}N_2$), 21.4 ($C_6H_4\underline{Me}$), 21.2 ($C_6H_4\underline{Me}$) ppm. IR (NaCl plates, Nujol mull, cm^{-1}): 1598 (w), 1277 (m), 1245 (w), 1212 (w), 1144 (m), 1088 (m), 1070 (m), 1052 (m), 1019 (w), 983 (m), 950.2 (m), 902.2 (m), 838 (m), 817 (w), 799 (w), 730 (m), 676 (m), 588 (m), 558 (m). Anal. Found (calcd for $C_{24}H_{34}AlN_3O_5S_2$): C, 53.68 (53.81); H, 6.36 (6.40); N, 7.74 (7.84).

General Procedure for Solution Polymerization of *rac*-LA. *rac*-LA (6.00 mmol) and catalyst (0.06 mmol) were added to a Schlenk flask and heated to 70 °C. To this was added hot (70 °C) toluene (6.0 mL), rapidly dissolving both solids. The resultant solution was heated at 70 °C and aliquots were taken via syringe at the respective time. Upon completion of the reaction, wet THF (10 mL) was added and the solution evaporated to dryness to give the poly(*rac*-LA). Conversions were determined by ^1H NMR integration of the $OC\underline{H}Me$ resonance relative intensities of the residual *rac*-LA and poly(*rac*-LA).

General Procedure for Solvent-Free (Melt) Polymerization of *rac*-LA. A Schlenk flask was charged with catalyst and *rac*-LA at the desired ratio and heated to 130 °C for 30 min with stirring. The mixture was cooled to RT, wet THF (10 mL) was then added, and the resulting solution was evaporated to dryness to give the crude polymer.

Crystal Structure Determinations of $H_2N_2{}^{Ts}N^{Ph}$ (15), $H_2N_2{}^{Ms}N^{Ph}$ (16), $Al(CyN_2{}^{Ts})Et(THF)$ (17), $Al(N_2{}^{Ts}N^{Ph})Et$ (19), $Al(N_2{}^{Ts}N^{OMe})Et$ (20), $Al(N_2{}^{Ts}N^{py})Et$ (21), $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (28), and $Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (30). X-ray data collection and processing parameters are given in Table S3 of the SI. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[103] The structures were solved with SIR92[104] or SHELXS-97,[105] and further refinements and all other crystallographic calculations were performed using either the CRYSTALS program suite[106] or SHELXS-97.[107] Other details of the structure solution and refinements are given in the SI (CIF data). A full listing of atomic coordinates, bond lengths and angles, and displacement parameters for all the structures have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Acknowledgment. We thank the EPSRC and Chinese Scholarship Council for support, and the Chemical Crystallography Laboratory, Oxford, for access to the KCCD diffractometers. We also thank Dr. A. L. Thompson for advice with regard to the crystallography and Miss K. Herbert for assistance with the synthesis of **16**.

Supporting Information Available: X-ray crystallographic data in CIF format for the structure determinations of $H_2N_2{}^{Ts}N^{Ph}$ (**15**), $H_2N_2{}^{Ms}N^{Ph}$ (**16**), $Al(CyN_2{}^{Ts})Et(THF)$ (**17**), $Al(N_2{}^{Ts}N^{Ph})Et$ (**19**), $Al(N_2{}^{Ts}N^{OMe})Et$ (**20**), $Al(N_2{}^{Ts}N^{py})Et$ (**21**), $[Al(N^{Ts}{}_2N^{Ph})Cl]_2$ (**28**), $Al(N_2{}^{Ts}N^{OMe})(OCH_2CH_2NH_2)$ (**30**), and $Al(OCH_2CH_2NH_2)Et_2$; preliminary structure determination of $[Al(N_2{}^{Ts}N^{O})]_2$ (**25**); displacement ellipsoid plot of $Al(OCH_2CH_2NH_2)Et_2$; additional data concerning the ROP catalysis; X-ray data collection and processing parameters. This information is available free of charge via the Internet at http://pubs.acs.org.

---

(103) Otwinowski, Z.; Minor, W. *Processing of X-ray Diffraction Data Collected in Oscillation Mode*; Academic Press: New York, 1997.

(104) Altomare, A.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(105) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

(106) Betteridge, P. W.; Cooper, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487.

(107) Sheldrick, G. M.; Schneider, T. R. *Methods Enzymol.* **1997**, *277*, 319–343.