

# Synthesis and Reactions of Aluminum Sulfonamide Alkyls and Hydride

Jian Zhao, Haibin Song, and Chunming Cui\*

State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Received December 14, 2006

Aluminum compounds supported by a sulfonamide ligand are described. Reaction of  $\text{AlEt}_3$  with 1 equiv of the sulfonyl amine  $\text{ArNH}(\text{SO}_2\text{-}p\text{-Tol})$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ,  $\text{Tol} = 4\text{-MeC}_6\text{H}_4$ ) yielded the dimeric aluminum species  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})\text{AlEt}_2]_2$  (**1**), and reactions of  $\text{AlEt}_3$  and  $\text{AlH}_3\cdot\text{NMe}_3$  with 2 equiv of  $\text{ArNH}(\text{SO}_2\text{-}p\text{-Tol})$  yielded the aluminum bis(sulfonamide) species  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlEt}$  (**2**) and  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlH}$  (**3**). The iodide species  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})\text{AlI}_2]_2$  (**4**) and  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlI}$  (**5**) were prepared by the reaction of **1** and **2** with iodine. Reaction of **3** with  $\text{PhNH}_2$ ,  $\text{HCCPh}$ , and  $\text{Ph}_2\text{CO}$  yielded  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlNHPH}$  (**6**),  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlCCPh}$  (**7**), and  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]_2\text{AlOCHPh}_2$  (**8**). Treatment of **6** with  $\text{Bu}^\text{n}\text{Li}$  in *n*-hexane led to a ligand transfer reaction to give the dimeric lithium salt  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})\text{Li}(\text{THF})_2]_2$  (**9**). Compounds **1–4** and **7–9** have been characterized by X-ray single-crystal analysis, which disclosed that the aluminum mono(sulfonamide) compounds adopt a dimeric NSOAINSOAl eight-membered-ring structure while the aluminum bis(sulfonamide) species are monomeric species with a five-coordinate aluminum center. Interestingly, the lithium salt **9** has a dimeric structure with an OSOLiOSOLi eight-membered-ring core. Compounds **3** and **8** are found to be active for lactide polymerization at high temperature.

## Introduction

Aluminum complexes supported by monoanionic bidentate ligands have been extensively investigated recently, since they are excellent precursors for the generation of well-defined cationic alkyls and low-valent aluminum species.<sup>1</sup> The key features of these ligands include electron delocalization in the ligand backbone to form chelating complexes and tunable electronic and steric properties by modification of substituents on the ligand backbone. Monoanionic sulfonamide ligands are also potential bidentate ligands, since the electron may be delocalized over oxygen, sulfur, and nitrogen atoms. In addition, because of the electron-withdrawing nature of sulfonyl groups, the derivatives of their amides are more acidic, similar to the case for phenols. As a result, metal sulfonamide complexes may display enhanced Lewis acidity compared to the normal amide complexes. In recent years, there has been growing interest in using chiral disulfonamide ligands as auxiliaries for the preparation of metal complexes as catalysts for organic transformations.<sup>2</sup> The first well-defined disulfonamide aluminum complex was reported in 1992 by Corey and co-workers and has been successfully applied as a catalyst for high enantioselective

Diels–Alder reactions.<sup>3</sup> Several main-group elements,<sup>4</sup> titanium,<sup>5</sup> and lanthanide complexes<sup>6</sup> supported by disulfonamide ligands have also been reported recently, and their structures have been investigated by X-ray single-crystal analysis. In view of the potential application of metal sulfonamide complexes in catalytic applications, we are interested in exploring the coordination behavior of this ligand family, since the corresponding structural data are still very limited. Herein we report on the synthesis and structures of aluminum and lithium complexes incorporating the bulky sulfonamide ligand  $[\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]^-$  ( $\text{Ar} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ,  $\text{Tol} = \text{toluene}$ )<sup>7</sup> and the subsequent reaction of the aluminum bis(sulfonamide) hydride with  $\text{PhNH}_2$ ,  $\text{Ph}_2\text{CO}$ , and  $\text{HCCPh}$ .

## Results and Discussion

### Synthesis of Aluminum Sulfonamide Alkyls and Hydride.

Reaction of the bulky sulfonamide ligand  $\text{ArNH}(\text{SO}_2\text{-}p\text{-Tol})$  with 1 equiv of  $\text{AlEt}_3$  in toluene at room temperature yielded  $(\text{LAlEt}_2)_2$  (**1**;  $\text{L} = [\text{ArN}(\text{SO}_2\text{-}p\text{-Tol})]^-$ ) (Scheme 1). The ethane and hydrogen elimination reactions of  $\text{AlEt}_3$  and  $\text{AlH}_3\cdot\text{NMe}_3$  with 2 equiv of  $\text{ArNH}(\text{SO}_2\text{-}p\text{-Tol})$  afforded the aluminum ethyl complex  $\text{L}_2\text{AlEt}$  (**2**) and the hydride  $\text{L}_2\text{AlH}$  (**3**), respectively. Alternatively, **2** can be also prepared quantitatively by the

\* To whom correspondence should be addressed. E-mail: cmcui@nankai.edu.cn.

(1) For leading references, see: (a) Coles, M. P.; Jordan, R. F. *J. Am. Chem. Soc.* **1997**, *119*, 8125. (b) Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1997**, *16*, 5183. (c) Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. *J. Am. Chem. Soc.* **1999**, *121*, 8673. (d) Aeilts, S. L.; Coles, M. P.; Swenson, D. C.; Jordan, R. F.; Young, V. G., Jr. *Organometallics* **1998**, *17*, 3265. (e) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070. (f) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274. (g) Schmidt, J. A. R.; Arnold, J. *Organometallics* **2002**, *21*, 2306.

(2) For examples, see: (a) Pritchett, S.; Woodmansee, D. H.; Gantzel, P.; Walsh, P. J. *J. Am. Chem. Soc.* **1998**, *120*, 6423. (b) Ackermann, L.; Bergman, R. G.; Loy, R. N. *J. Am. Chem. Soc.* **2003**, *125*, 11956. (c) Evans, D. A.; Nelson, S. G. *J. Am. Chem. Soc.* **1997**, *119*, 6452. (d) Seidel, S. W.; Deming, T. J. *Macromolecules* **2003**, *36*, 969.

(3) (a) Corey, E. J.; Sarshar, S.; Bordner, J. J. *Am. Chem. Soc.* **1992**, *114*, 7938. (b) Corey, E. J.; Sarshar, S.; Lee, D.-H. *J. Am. Chem. Soc.* **1994**, *116*, 12089.

(4) (a) Blaschette, A.; Michalides, A.; Jones, P. G. *J. Organomet. Chem.* **1991**, *411*, 57. (b) Kavallieratos, K.; Rosenberg, J. M.; Bryan, J. C. *Inorg. Chem.* **2005**, *44*, 2573.

(5) Royo, E.; Betancort, J. M.; Davis, T. J.; Carroll, P.; Walsh, P. J. *Organometallics* **2000**, *19*, 4840.

(6) Gorlitzer, H. W.; Spiegler, M.; Anwander, R. *Eur. J. Inorg. Chem.* **1998**, 1009.

(7) Carver, F. J.; Hunter, C. A.; Livingstone, D. J.; McCabe, J. F.; Seward, E. M. *Chem. Eur. J.* **2002**, *8*, 2848.

## Scheme 1. Synthesis of Aluminum Complexes

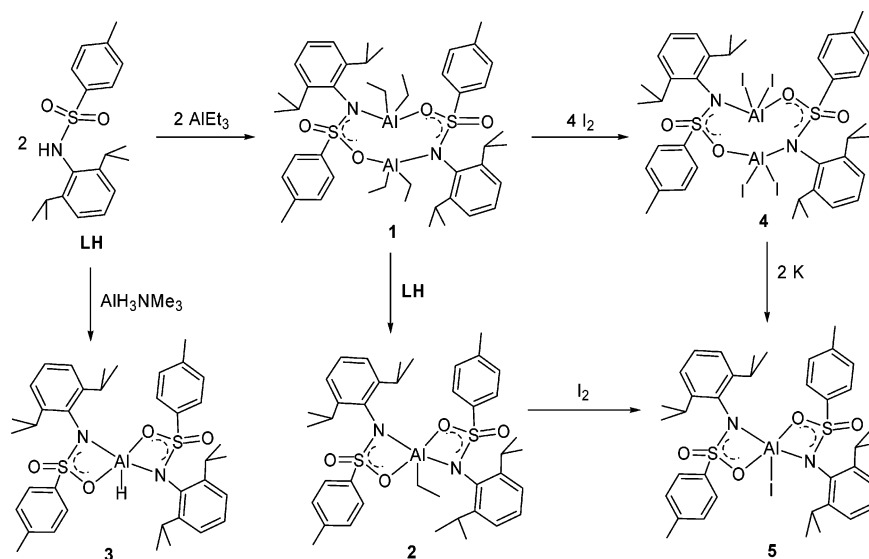


Table 1. Crystallographic Details for 1–3

	1	2	3·2C <sub>7</sub> H <sub>8</sub>
formula	C <sub>46</sub> H <sub>74</sub> Al <sub>2</sub> N <sub>2</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>40</sub> H <sub>53</sub> AlN <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>52</sub> H <sub>65</sub> AlN <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
formula wt	869.15	716.94	873.16
temp (K)	293(2)	294(2)	294(2)
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	10.5056(15)	11.1065(14)	30.430(6)
<i>b</i> (Å)	10.8810(15)	16.532(2)	9.810(2)
<i>c</i> (Å)	12.6463(18)	22.444(3)	21.250(4)
$\alpha$ (deg)	96.918(2)	89.462(2)	90
$\beta$ (deg)	99.860(2)	78.601(2)	126.940(8)
$\gamma$ (deg)	107.204(2)	88.062(2)	90
<i>V</i> (Å <sup>3</sup> )	1337.9(3)	4037.4(9)	5070.1(17)
<i>Z</i>	1	4	4
cryst dimens (mm)	0.14 × 0.12 × 0.08	0.38 × 0.32 × 0.26	0.24 × 0.22 × 0.18
<i>d</i> <sub>calcd.</sub> (g/cm <sup>3</sup> )	1.079	1.179	1.144
no. of rflns	7322	22 763	10 364
no. of obsd rflns	4661	16 125	4424
GOF	1.078	0.985	1.051
R1 ( <i>I</i> > 2σ( <i>I</i> ))	0.0753	0.0540	0.0619
wR2 (all)	0.2742	0.1523	0.2091

reaction of **1** with 1 equiv of ArNH(SO<sub>2</sub>-*p*-Tol) in toluene at room temperature. It is noteworthy that reaction of ArNH(SO<sub>2</sub>-*p*-Tol) with 1 equiv of AlH<sub>3</sub>NMe<sub>3</sub> did not give the desired (LAlH<sub>2</sub>)<sub>2</sub>; instead, L<sub>2</sub>AlH was isolated along with an excess of sulfonamide under various conditions. Compounds **1**–**3** were isolated as colorless crystals by crystallization from toluene. They have been characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra, and elemental analysis. The structures of these compounds were determined by X-ray single-crystal analysis. Crystal data for **1**–**3** are summarized in Table 1. The molecular structures of **1**–**3** are shown in Figures 1–3, respectively.

The structure of **1** has a crystallographically required center of symmetry with a bimetallic Al<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> eight-membered ring in a chair conformation. The two bridging sulfonamide ligands link the two AlEt<sub>2</sub> units. The central aluminum atoms are four-coordinated and adopt a distorted-tetrahedral geometry, being bonded to two ethyl groups and to one of the two oxygen atoms and the nitrogen atom in the ligand. The Al–C bond lengths (1.949(5) Å) are in the range for an Al–C single bond. The structure may be comparable to those of the dimeric amidinate complex {[MeC(NMe)<sub>2</sub>]AlMe<sub>2</sub>}<sub>2</sub><sup>8</sup> and amide complex {[Me<sub>2</sub>Al[μ,η<sup>2</sup>-ArNC(Ph)O]}<sub>2</sub>.<sup>9</sup> The Al–N bond length (1.944(3) Å) is

just out of the range reported for aluminum mono(amidinate) alkyls (1.912–1.940 Å) but shorter than those found in the dimeric amidato species {[Me<sub>2</sub>Al[μ,η<sup>2</sup>-ArNC(Ph)O]}<sub>2</sub> (1.973(1) Å).<sup>9</sup> The Al–O bond lengths (1.882(3) Å) are significantly longer than those in {[Me<sub>2</sub>Al[μ,η<sup>2</sup>-ArNC(Ph)O]}<sub>2</sub> (1.811(1) Å).<sup>10</sup> The S1–O1 (1.480(3) Å) and S1–N1 (1.581(3) Å) are longer than those of normal S=O (1.40–1.44 Å) and S=N double bonds (ca. 1.50 Å).<sup>11</sup> The lengthening of the S–O and S–N distances indicates the delocalized bonding of the N–S–O backbone to the aluminum atoms.

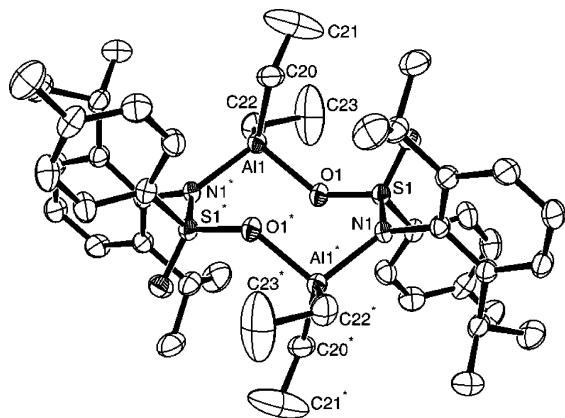
Single crystals of **2** and **3** suitable for X-ray analysis were obtained from toluene. The structure of **2** is crystallographically centrosymmetric. Both compounds are monomeric, and the central aluminum atom is five-coordinated. The geometry of the aluminum atom can be best described as distorted trigonal bipyramids (tbp) in which the two bonded oxygen atoms of the sulfonamide ligands occupy axial sites and equatorial sites are occupied by the methylene carbon atom and two nitrogen atoms of the ligands. The sum of the equatorial atomic angles (357.96° in **2**) is close to 360°, but the O–Al–O angles (155.21(10)° in **2** and 160.83(16)° in **3**) markedly deviate from the ideal linearity for a tbp because of the acute N–Al–O angles (from 71.84(9) to 72.56(10)°). The wide O–Al–O angles and high coordination number of **2** and **3** lead to the relatively longer Al–O bond lengths (1.975(2) and 1.982(2) Å in **2** and 2.000(2) Å in **3**) compared to those found in **1**. The Al–N bond lengths in **2** (1.930(3) and 1.933(2) Å) are longer than the corresponding Al–N distances in **3** (1.899(3) Å) but are in the reported range for aluminum bis(amidinate) alkyl complexes (1.914–1.986 Å).<sup>1b</sup> The Al–C bond length (1.954(3) Å) in **2** is typical for an Al–C bond found in the five-coordinate aluminum alkyls. The N–S (1.589–1.619 Å) and O–S bond lengths (1.491–1.4996 Å) in the bonding backbone are slightly lengthened compared to those found in **1**. These structural parameters indicate the charge delocalization in the N–S–O subunit and the bonding mode of the sulfonamide ligand can be rationalized as a chelating coordination.

(8) Hausen, H.-D.; Gerstner, F.; Schwartz, W. *J. Organomet. Chem.* **1978**, *145*, 277.

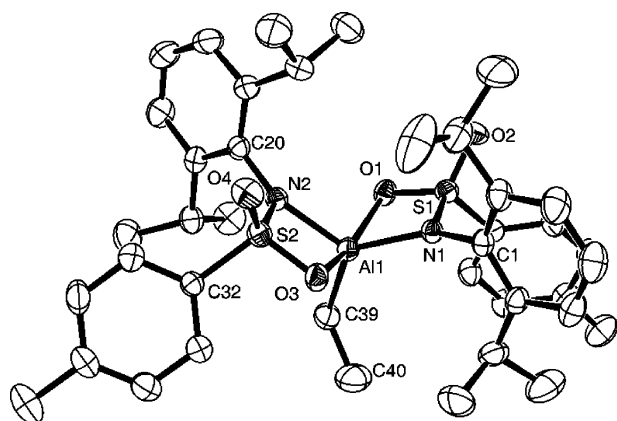
(9) Huang, B. H.; Yu, T. L.; Huang, Y. L.; Ko, B. T.; Lin, C. C. *Inorg. Chem.* **2002**, *41*, 2987.

(10) Huang, Y. L.; Huang, B. H.; Ko, B. T.; Lin, C. C. *Dalton Trans.* **2001**, 1390.

(11) Blais, P.; Brask, J. K.; Chivers, T.; Schatte, G. *Inorg. Chem.* **2001**, *40*, 384.

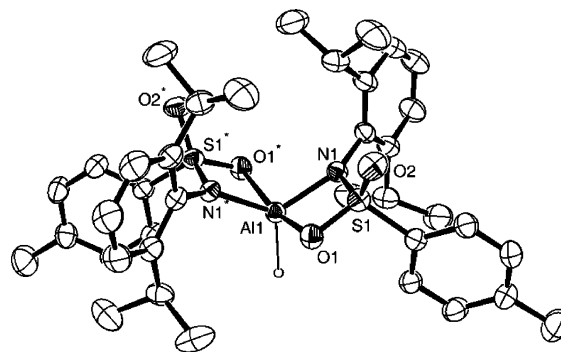


**Figure 1.** Ortep drawing of **1** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–O1 = 1.882(3), Al1–N1\* = 1.944(3), Al1–C22 = 1.949(5), Al1–C20 = 1.962(5), S1–O1 = 1.480(3), S1–N1 = 1.581(3); O1–Al1–N1\* = 101.37(14), O1–Al1–C22 = 103.81(19), N1\*–Al1–C22 = 109.90(19), O1–Al1–C20 = 108.71(18), C22–Al1–C20 = 117.9(2), O1–S1–N1 = 104.48(16), S1–O1–Al1 = 137.64(19), S1–N1–Al1\* = 122.22(18).

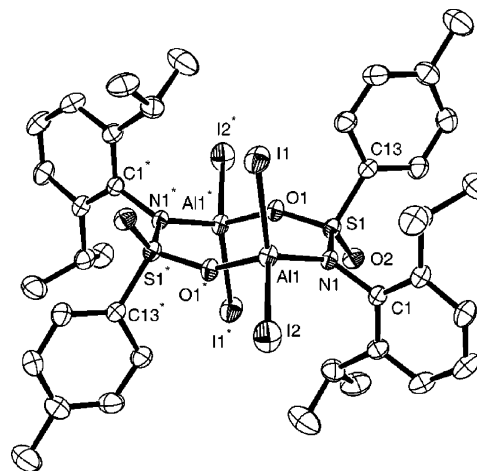


**Figure 2.** Ortep drawing of **2** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–N2 = 1.930(3), Al1–N1 = 1.933(2), Al1–C39 = 1.954(3), Al1–O3 = 1.975(2), Al1–O1 = 1.982(2), S1–O1 = 1.487(2), S1–O2 = 1.422(2), S1–N1 = 1.589(2), S2–O3 = 1.492(2), S2–O4 = 1.423(2), C39–C40 = 1.495(5); N2–Al1–N1 = 123.74(11), N2–Al1–C39 = 112.01(13), N1–Al1–C39 = 124.22(13), N2–Al1–O3 = 72.24(10), N1–Al1–O3 = 94.97(10), N2–Al1–O1 = 97.25(10), N1–Al1–O1 = 71.84(9), O3–Al1–O1 = 155.21(10), O1–S1–N1 = 96.57(12), S1–N1–Al1 = 94.90(12), S2–N2–Al1 = 94.68(12), S1–O1–Al1 = 96.30(11), S2–O3–Al1 = 95.92(11).

The  $^1\text{H}$  NMR spectra of **2** and **3** contain four doublets for the resonances of the  $\text{CHMe}_2$  groups. One of the doublets is shifted significantly upfield ( $\delta$  0.25 in **2** and 0.26 ppm in **3**) because of the close intramolecular contact (the closest  $\text{H}-\text{C}_{\text{Ph}}$  distance is 2.937 Å) of one of the methyl groups with the S-bound phenyl rings, as observed in the crystal structures of **2** and **3**. The broad Al–C resonance of **2** was found at  $\delta$  0.60 ppm in the  $^{13}\text{C}$  NMR spectrum. The terminal hydride resonance in **3** was not observed in the  $^1\text{H}$  NMR spectrum, but its existence was unambiguously verified by the solid-state IR spectrum, in which the strong band centered at  $1865\text{ cm}^{-1}$  is characteristic of Al–H vibration absorptions.<sup>12</sup>



**Figure 3.** Ortep drawing of **3** (30% probability). Hydrogen atoms, except that attached to the aluminum atom, have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–N1 = 1.899(3), Al1–O1 = 2.000(2), Al1–S1 = 2.6153(10), Al1–H1 = 1.86(5), S1–O1 = 1.491(2), S1–O2 = 1.409(2), S1–N1 = 1.619(3); N1\*–Al1–N1 = 121.70(17), N1–Al1–O1\* = 97.90(11), N1–Al1–O1 = 72.56(10), O1\*–Al1–O1 = 160.83(16), O1–S1–N1 = 95.75(13), S1–N1–Al1 = 95.71(13), S1–O1–Al1 = 95.92(12).



**Figure 4.** Ortep drawing of **4** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Al1–O1\* = 1.808(4), Al1–N1 = 1.872(5), Al1–I2 = 2.4858(19), Al1–I1 = 2.5065(19), S1–O1 = 1.501(4), S1–N1 = 1.595(5), O1–Al1\* = 1.808(4), N1–C1 = 1.483(7), S1–C13 = 1.744(16); O1\*–Al1–N1 = 105.1(2), O1\*–Al1–I2 = 104.73(16), N1–Al1–I2 = 112.23(16), O1\*–Al1–I1 = 110.15(15), N1–Al1–I1 = 113.26(17), I2–Al1–I1 = 110.88(7), O1–S1–N1 = 101.5(2), S1–O1–Al1\* = 140.0(3).

**Reaction of 1 and 2 with Iodine.** It is known that aluminum iodides can be prepared by the reaction of the corresponding aluminum methyl species with iodine.<sup>12</sup> The reaction of the aluminum mono- and bis(sulfonamide) ethyl species with the appropriate amount of iodine in toluene afforded the expected iodides  $(\text{LAlI}_2)_2$  (**4**) and  $\text{L}_2\text{AlI}$  (**5**) in good yield. Both compounds were isolated as colorless crystals from toluene. Reduction of **4** with potassium did not give the desired low valent species but resulted in the formation of **5**. Similar reduction of **5** yielded a complicated mixture, which could not be separated and characterized.

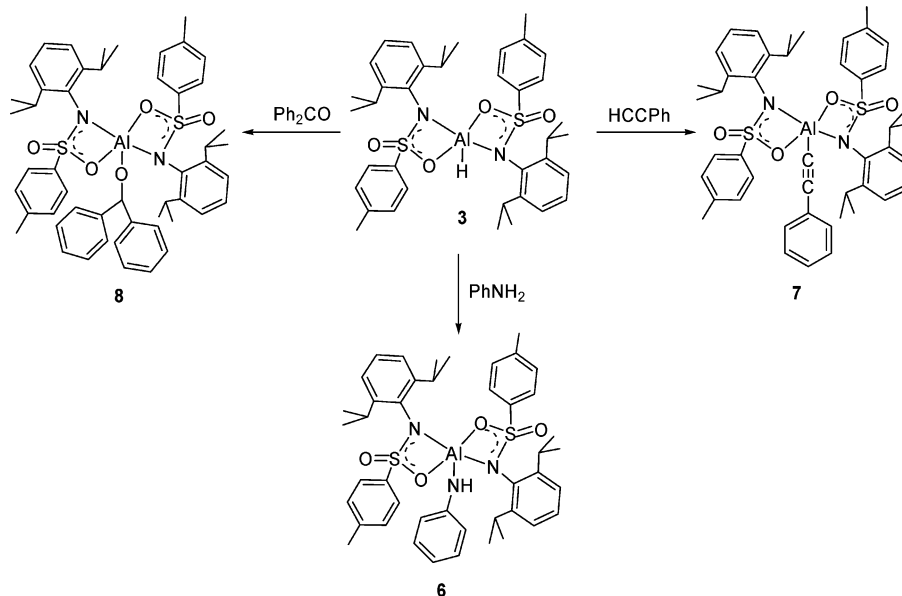
The molecular structure of **4** has been determined by X-ray single crystal analysis, which is shown in Figure 4 along with selected bond parameters. Crystal data for **4** are summarized in Table 2. Compound **4** is dimeric, and the overall structure is similar to that of **1**. The Al–O and Al–N bond lengths (1.808(4) and 1.872(5) Å) in **4** are much shorter than those found in **1** (1.882(3) Å) because of the electron-withdrawing nature of the

(12) (a) Wang, X.; Andrews, L.; Tam, S.; DeRose, M. E.; Fajardo, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 9218. (b) Himmel, H.-J.; Vollet, J. *Organometallics* **2002**, *21*, 5972. (c) Chang, J.-C.; Hung, C.-H.; Huang, J.-H. *Organometallics* **2001**, *20*, 4445.

Table 2. Crystallographic Details for 4 and 7–9

	4	7	8-C <sub>7</sub> H <sub>8</sub>	9
formula	C <sub>26</sub> H <sub>32</sub> AlI <sub>2</sub> NO <sub>2</sub> S	C <sub>46</sub> H <sub>53</sub> AlN <sub>2</sub> O <sub>4</sub> S <sub>2</sub>	C <sub>58</sub> H <sub>67</sub> AlN <sub>2</sub> O <sub>5</sub> S <sub>2</sub>	C <sub>54</sub> H <sub>64</sub> Li <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub>
formula weight	703.37	789.00	963.24	947.07
temp (K)	294(2)	113(2)	113(2)	293(2)
cryst syst	triclinic	tetragonal	trigonal	triclinic
space group	<i>P</i> $\bar{1}$	<i>I</i> <sub>4</sub> / <i>a</i>	<i>R</i> 3:H	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.2632(17)	40.2284(5)	46.107(3)	11.270(3)
<i>b</i> (Å)	12.263(2)	40.2284(5)	46.107(3)	11.371(3)
<i>c</i> (Å)	12.986(2)	10.69300(10)	13.1715(12)	12.802(3)
$\alpha$ (deg)	89.811(3)	90	90	77.355(4)
$\beta$ (deg)	76.040(3)	90	90	75.431(4)
$\gamma$ (deg)	69.851(3)	90	120	65.187(4)
<i>V</i> (Å <sup>3</sup> )	1483.4(4)	17 304.7(3)	24 250(3)	1429.2(6)
<i>Z</i>	2	16	18	1
cryst dimens, mm	0.40 × 0.38 × 0.34	0.32 × 0.28 × 0.24	0.12 × 0.06 × 0.04	0.26 × 0.24 × 0.18
<i>d</i> <sub>calcd</sub> (g/cm <sup>3</sup> )	1.575	1.211	1.187	1.100
no. of rflns	8403	74 564	61 704	7297
no. of obsd rflns	5982	10 273	9491	5020
GOF	1.025	1.085	1.285	1.035
R1 ( <i>I</i> > 2σ( <i>I</i> ))	0.0501	0.0482	0.1206	0.0620
wR2 (all)	0.1654	0.1193	0.2192	0.2138

Scheme 2. Reactions of the Hydride 3



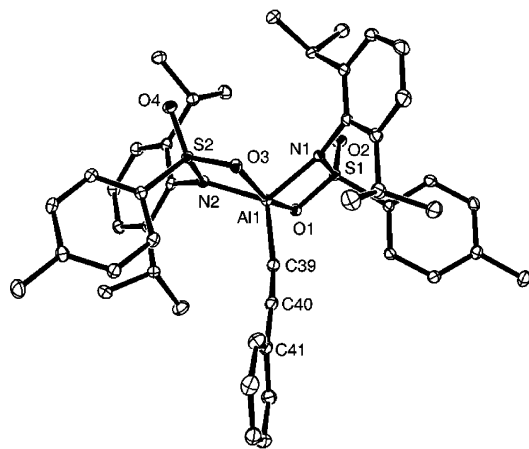
iodide ligands. As a result, the S1–O1 (1.501(4) Å) bond length in 4 is lengthened by 0.021 Å compared to those in 4 (1.480(3) Å). The O1–S1–N1 angle (104.48(16)°) in 1 is also slightly more open than those (101.5(2)°) in 4.

**Reaction of 3 with NH<sub>2</sub>Ph, HCCPh, and Ph<sub>2</sub>CO.** Aluminum hydrides are highly reactive and have been used as reducing agents for carbonyls, imines, and other unsaturated functional groups because of the nucleophilic nature of hydride ligands. Aluminum hydrides also undergo hydrogen elimination reactions with alcohols, amines, and terminal acetylenes.<sup>13,14</sup> The five-coordinate aluminum hydride 3 is thermally stable in solution and in the solid state and does not decompose in refluxing toluene within 2 h and in the melt (ca. 245 °C). The high thermal

stability of 3 is comparable to that of the amidinate hydride [ArNC(H)NAr]<sub>2</sub>AlH.<sup>13a</sup> However, it has been shown that the monomeric aluminum hydrides [C<sub>4</sub>H<sub>3</sub>N(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>AlH and (OCCMeCHCMeNAr)<sub>2</sub>AlH with five- and six-membered rings are not stable in solution and decompose at 70–80 °C. 3 is highly reactive and could be used as a precursor for the preparation of the amide L<sub>2</sub>AlNHPH (6), alkynyl L<sub>2</sub>AlCCPh (7), and alkoxide L<sub>2</sub>AlOCHPh<sub>2</sub> (8) by reactions with PhNH<sub>2</sub>, HCCPh, and Ph<sub>2</sub>CO, respectively (Scheme 2). All of these compounds have been characterized by IR, <sup>1</sup>H and <sup>13</sup>C NMR, and elemental analysis. The molecular structures of 7 and 8 have been determined by X-ray single-crystal analysis. These five-coordinate aluminum species show NMR patterns in the ligand region similar to those observed in the NMR spectra of L<sub>2</sub>AlH (3). The <sup>1</sup>H NMR spectrum of 6 displayed a singlet at δ 3.57 ppm, attributed to the resonance of the amide proton, which was further supported by its IR spectrum, in which the N–H stretching vibration appeared at 3440 cm<sup>-1</sup>. The <sup>13</sup>C NMR spectrum of 7 shows characteristic resonances at δ 109.8 and 106.5 ppm for the C≡C moiety, comparable to those found in Bu<sub>2</sub>pzAlCCPh (3,5-Bu<sub>2</sub>pz = 3,5-di-*tert*-butylpyrazolate).<sup>14</sup>

(13) (a) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1998**, *37*, 6906. (b) Cole, M. L.; Jones, C.; Junk, P. C.; Kloth, M.; Stasch, A. *Chem. Eur. J.* **2005**, *11*, 4482. (c) Lin, C.-Y.; Tsai, C.-F.; Chen, H.-J.; Hung, C.-H.; Yu, R.-C.; Kuo, P.-C.; Lee, H. M.; Huang, J.-H. *Chem. Eur. J.* **2006**, *12*, 3067. (d) Kuo, P.-H.; Chen, I.-C.; Chang, J.-C.; Lee, M.-T.; Hu, C.-H.; Hung, C.-H.; Lee, H. M.; Huang, J.-H. *Eur. J. Inorg. Chem.* **2004**, 4898. (14) (a) Zheng, W.; Hohmeister, H.; Möscher-Zanetti, N. C.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2001**, *40*, 2363. (b) Zheng, W.; Möscher-Zanetti, N. C.; Roesky, H. W.; Hewitt, M.; Cimpoesu, F.; Schneider, T. R.; Stasch, A.; Prust, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3099. (c) Himmel, H.-J. *Organometallics* **2003**, *22*, 2679.



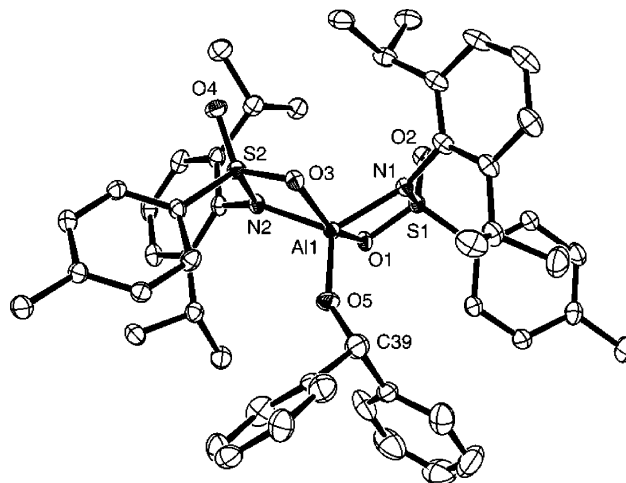


**Figure 5.** Ortep drawing of **7** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S1–O1 = 1.4996(12), S1–O2 = 1.4279(12), S1–N1 = 1.5947(14), S2–O3 = 1.4933(12), S2–O4 = 1.4321(12), S2–N2 = 1.5967(13), Al1–N1 = 1.8942(14), Al1–N2 = 1.8980(14), Al1–C39 = 1.9332(18), Al1–O1 = 1.9591(12), Al1–O3 = 1.9817(12), C39–C40 = 1.210(2); O1–S1–N1 = 96.08(7), O3–S2–N2 = 96.23(7), N1–Al1–N2 = 120.80(6), N1–Al1–O1 = 73.35(5), N1–Al1–O3 = 93.89(5), N2–Al1–O3 = 72.73(5), C39–Al1–O3 = 97.54(6), S1–O1–Al1 = 95.48(6), S2–O3–Al1 = 95.54(6), S2–N2–Al1 = 95.47(7), C40–C39–Al1 = 167.43(15), C39–C40–C41 = 173.23(18).

Single crystals of **7** were obtained from toluene. The molecular structure of **7** is shown in Figure 5 along with selected bond lengths and angles. Compound **7** is monomeric in the solid state. The overall structure is comparable to those of **2** and **3**. Compound **7** features a terminal acetylide ligand. The Al–C bond length in **7** (1.9332(18) Å) is longer than those found in the four-coordinate aluminum acetylide species [3,5-Bu<sub>2</sub>pz(μ-Al)<sub>2</sub>(CCPh)<sub>2</sub>]<sub>2</sub> (1.913(3) and 1.929 Å). The short C39–C40 bond distance (1.210(2) Å) indicates a C–C triple bond. The Al1–C39–C40 bond angle (167.43(15)°) significantly deviates from linearity compared to those in a few known terminal acetylide aluminum compounds (174.3–178.2°), probably caused by the hydrogen bonding of one of the 2-H atoms of the S-bound phenyl ring with the C40 (the H–C39 and H–C40 distances are 2.724 and 2.734 Å). This kind of abnormal deviation, however, has been previously observed in the structure of [3,5-Bu<sub>2</sub>pz(μ-Al)<sub>2</sub>(CCPh)<sub>2</sub>]<sub>2</sub>.<sup>14</sup>

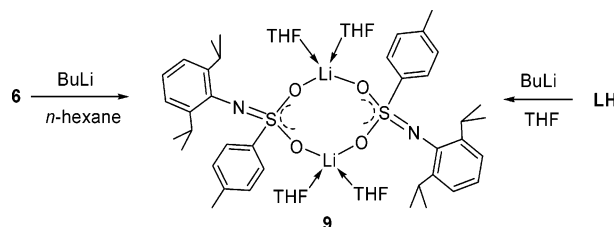
Compound **8** is stable in solution and in the solid state at ambient temperature. However, it slowly decomposes (ca. 10% within 6 h) in refluxing toluene, leading to the formation of the free ligand. Single crystals of **8** suitable for X-ray analysis were obtained from toluene. The structure is shown in Figure 6. Compound **8** also has a monomeric structure with a five-coordinate aluminum center (Figure 6) similar to those of **2**, **3**, and **7**. The Al1–O5 bond length (1.699(4) Å) is short and consistent with the corresponding distances found in terminal aluminum alkoxides.<sup>15</sup>

**Generation of Lithium Sulfonamide.** Compound **6** has a terminal hydroamino group. We reasoned that deprotonation with BuLi might yield the corresponding binuclear species. The reaction of **6** with Bu<sup>n</sup>Li in *n*-hexane at room temperature gave a white precipitate, which is not soluble in hydrocarbon solvents



**Figure 6.** Ortep drawing of **8** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S1–O1 = 1.499(3), S1–O2 = 1.433(4), S1–N1 = 1.593(4), S2–O3 = 1.496(4), S2–O4 = 1.430(4), S2–N2 = 1.591(4), Al1–N1 = 1.899(4), Al1–N2 = 1.914(4), Al1–O5 = 1.699(4), Al1–O1 = 1.966(4), Al1–O3 = 1.963(4), O5–C39 = 1.372(7); O1–S1–N1 = 95.9(2), O3–S2–N2 = 96.5(2), N1–Al1–N2 = 126.51(19), N1–Al1–O1 = 72.90(16), N1–Al1–O3 = 95.03(16), N2–Al1–O3 = 72.90(16), O5–Al1–O3 = 101.97(18), S1–O1–Al1 = 95.82(18), S2–O3–Al1 = 95.77(18), S2–N2–Al1 = 94.6(2), C39–O5–Al1 = 146.3(4).

### Scheme 3. Synthesis of Lithium Complex **9**

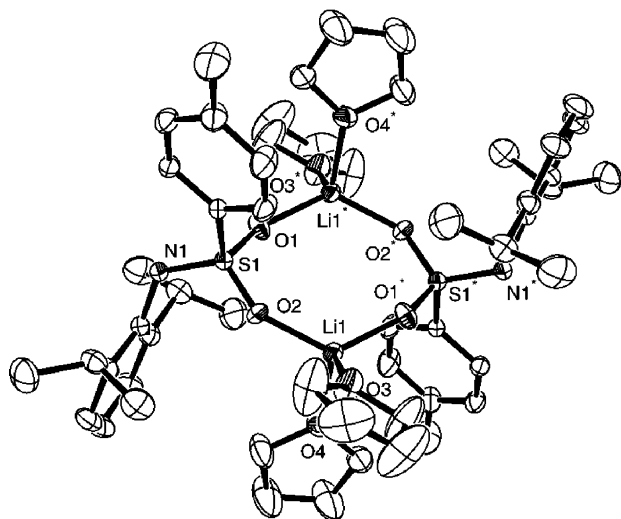


(Scheme 3). Colorless crystals of the product were grown from THF, and its structure was determined by X-ray single-crystal analysis. The lithium mono(sulfonamide) salt **9** has a dimeric structure with a Li<sub>2</sub>O<sub>4</sub>S<sub>2</sub> eight-membered ring having a crystallographic central symmetry (Figure 7). In this case, the lithium ion is coordinated to the two oxygen atoms in the ligand. The central lithium atoms in **9** are four-coordinated. The average Li–O bond length in the eight-membered ring is 1.881(6) Å, which is very close to those found in polymeric [Li(THF)<sub>2</sub>{Al-[SO<sub>2</sub>(NBu<sup>n</sup>)<sub>2</sub>]}]<sub>∞</sub>.<sup>11</sup> The S–O bond length of 1.463(2) Å is slightly longer than a typical S=O double bond. The S–N bond length (1.520(3) Å) indicates a double-bond character. Very few lithium sulfonamides have been structurally characterized.<sup>16</sup> The closely related mono((trifluoromethyl)sulfonyl)amide [Li(CF<sub>3</sub>-SO<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>OCH<sub>3</sub>)]<sub>2</sub>·CH<sub>3</sub>CN adopts a dimeric structure with μ<sub>2</sub>(O,N) coordination.<sup>16a</sup> The unusual bridging μ<sub>2</sub>(O,O) coordination in the structure of **9** may result from the sterically demanding Ar groups.

**Lactide Polymerization Reactions.** Aluminum alkoxides are known to be excellent initiators for lactide polymerization reactions.<sup>17</sup> The stereoselectivity of aluminum precursors depends largely on the ligand systems employed. Therefore, catalytic behaviors of the hydride **3** and alkoxide **8** for lactide

(15) (a) Wengrovius, J. H.; Garbaskas, M. F.; Williams, E. A.; Going, R. C.; Donahue, P. E.; Smith, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 982. (b) Healy, M. D.; Power, M. B.; Barron, A. R. *Coord. Chem. Rev.* **1994**, *130*, 63. (c) Lewiński, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789. (d) Amgoune, A.; Lavanant, L.; Thomas, C. M.; Chi, Y.; Welter, R.; Dagorne, S.; Carpentier, J.-F. *Organometallics* **2005**, *24*, 6279.

(16) (a) Dillon, R. E. A.; Stern, C. L.; Shriver, D. F. *Chem. Mater.* **2000**, *12*, 1122. (b) Brouillette, D.; Irish, D. E.; Taylor, N. J.; Perron, G.; Odziemkowski, M.; Desnoyers, J. E. *Phys. Chem. Chem. Phys.* **2002**, *4*, 6063.



**Figure 7.** Ortep drawing of **9** (30% probability). Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): S1–O1 = 1.463(2), S1–O2 = 1.464(2), S1–N1 = 1.520(3), O2–Li1 = 1.866(6), O3–Li1 = 1.983(6), O4–Li1 = 1.969(6), Li1–O1\* = 1.881(6); O1–S1–O2 = 110.67(16), O1–S1–N1 = 115.25(15), O2–S1–N1 = 115.55(15), S1–O1–Li1\* = 148.7(2), S1–O2–Li1 = 145.6(2), O2–Li1–O1\* = 124.8(3), O2–Li1–O4 = 105.3(3), O1\*–Li1–O4 = 111.0(3), O2–Li1–O3 = 105.3(3), O1\*–Li1–O3 = 105.0(3), O4–Li1–O3 = 103.3(3).

**Table 3.** Solution Polymerization of D,L-Lactide

entry	cat. <sup>a</sup>	time (h)	<i>T</i> (°C) <sup>b</sup>	conversion (%) <sup>c</sup>	<i>M</i> <sub>w</sub> <sup>d</sup>	<i>M</i> <sub>n</sub> <sup>d</sup>	PDI <sup>d</sup>
1	L <sub>2</sub> AlOCHPh <sub>2</sub>	10	70	40	nd	nd	nd
2	L <sub>2</sub> AlOCHPh <sub>2</sub>	10	130	91	9776	6232	1.56
3	L <sub>2</sub> AlH	10	130	85	7945	5426	1.46

<sup>a</sup> Conditions: 20 mL of toluene solvent, 1.44 g of D,L-lactide, [LA]/[Al] = 100. <sup>b</sup> Oil bath temperature. <sup>c</sup> Conversion determined via <sup>1</sup>H NMR. <sup>d</sup> The weight average molecular weights (*M*<sub>w</sub>), the number average molecular weights (*M*<sub>n</sub>), and the polydispersity indices (PDI = *M*<sub>w</sub>/*M*<sub>n</sub>) were determined by GPC. nd = not determined.

polymerization have been examined. Both compounds have low catalytic activity at high temperatures (70–130 °C) to give low-molecular-weight polylactides with relatively narrow molecular weight distributions (Table 3). The experimental results show that the alkoxide **8** is more efficient than the corresponding hydride species. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra of the PLAs indicate the formation of atactic polymers.

### Conclusion

Three bonding modes have been observed in the aluminum and lithium sulfonamide complexes. The ligand displays a  $\mu_2$  coordination mode in mono(sulfonamide) aluminum complexes and an  $\eta^2$ -coordination mode in bis(sulfonamide) complexes. The sulfonamide ligand in these aluminum complexes shows remarkable electron delocalization over the N–S–O backbone. The lithium complex shows an unusual  $\mu_2$  coordination with the two oxygen atoms of the ligand attached to the lithium ions. This study demonstrates that by employing steric demanding substituents on the sulfonamide ligand backbone it is possible to isolate mononuclear metal sulfonamide complexes and that sulfonamides are potentially useful as spectator chelating ligands.

### Experimental Section

**General Remarks.** All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately before use. The chemicals used in this study were purchased from Aldrich or Acros and used as received. ArNH(SO<sub>2</sub>-*p*-Tol) was prepared as described in the literature.<sup>7</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data were recorded on a Varian Mercury Plus 400 spectrometer. IR spectra were recorded on a Bio-Rad FTS 6000 spectrometer. Elemental analyses were carried out on an Elemental Vario EL analyzer.

**[ArN(SO<sub>2</sub>-*p*-Tol)AlEt<sub>2</sub>]<sub>2</sub> (**1**).** To a stirred solution of ArNH(SO<sub>2</sub>-*p*-Tol) (9.93 g, 30.0 mmol) in toluene (50 mL) was added AlEt<sub>3</sub> (4.5 mL, 32.9 mmol) over a period of 10 min. The mixture was stirred at room temperature for 4 h. The clear solution was concentrated (to 10 mL) and stored at –25 °C overnight, affording colorless crystals of **1** (11.46 g, 92%). Mp: 224–226 °C. Anal. Calcd for C<sub>46</sub>H<sub>68</sub>Al<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (830.43): C, 66.47; H, 8.25; N, 3.37. Found: C, 66.09; H, 7.80; N, 3.37. <sup>1</sup>H NMR (400.15 MHz, DMSO):  $\delta$  7.60 (d, 4H, Ar H), 7.37 (d, 4H, Ar H), 7.22 (t, 2H, Ar H), 7.09 (d, 4H, Ar H), 3.11 (sept, *J* = 6.80 Hz, 4H, CHMe<sub>2</sub>), 2.34 (s, 6H, PhMe), 1.44 (d, *J* = 6.80 Hz, 12H, CHMe<sub>2</sub>), 0.92 (d, *J* = 6.80 Hz, 12H, CHMe<sub>2</sub>), 0.97 (m, 12H, CH<sub>2</sub>CH<sub>3</sub>), –0.20 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>), –0.32 (m, 4H, CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100.63 MHz, DMSO):  $\delta$  148.2, 141.9, 139.5, 129.1, 128.8, 128.1, 126.8, 123.5 (Ar C), 27.7 (CHMe<sub>2</sub>), 24.0 (CHMe<sub>2</sub>), 20.8 (CMe), 9.7 (AlCH<sub>2</sub>CH<sub>3</sub>), 9.5 (AlCH<sub>2</sub>CH<sub>3</sub>), 9.4 (AlCH<sub>2</sub>CH<sub>3</sub>), 0.7 (AlCH<sub>2</sub>CH<sub>3</sub>). IR (cm<sup>–1</sup>): 3648 (m), 3260 (m), 3056 (m), 2926 (s), 2930 (s), 2865 (s), 1596 (m), 1494 (m), 1461 (m), 1441 (m), 1421 (m), 1382 (m), 1318 (m), 1282 (s), 1159 (s), 1108 (s), 1071(s), 1019 (m), 955 (s), 886 (m), 871 (m), 799 (s), 736 (m), 716 (m), 674 (s), 651 (m), 631 (m), 561 (s), 529 (m), 471 (m), 422 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)AlEt] (**2**).** A mixture of **1** (0.42 g, 1.0 mmol) and ArNH(SO<sub>2</sub>-*p*-Tol) (0.33 g, 1.0 mmol) in toluene (20 mL) was stirred at room temperature for 24 h. The volatiles were removed under vacuum to yield a white solid of **2** (0.72 g, 100%). Crystals of **2** were obtained from toluene at room temperature. Mp: 267–268 °C. Anal. Calcd for C<sub>40</sub>H<sub>53</sub>AlN<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (716.33): C, 67.01; H, 7.45; N, 3.91. Found: C, 66.91; H, 7.54; N, 3.55. <sup>1</sup>H NMR (400.15 MHz, CDCl<sub>3</sub>):  $\delta$  7.40 (d, 4H, Ar H), 7.22 (d, 2H, Ar H), 7.13 (t, 2H, Ar H), 7.09 (d, 4H, Ar H), 6.88 (d, 2H, Ar H), 4.14 (sept, *J* = 6.80 Hz, 2H, CHMe<sub>2</sub>), 2.80 (sept, *J* = 6.80 Hz, 2H, CHMe<sub>2</sub>), 2.25 (s, 6H, PhMe), 1.44 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>), 1.31 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>), 1.22 (t, *J* = 8.0 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.95 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>), 0.46 (m, *J* = 8.2 Hz, 2H, CH<sub>2</sub>CH<sub>3</sub>), 0.25 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>). <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>):  $\delta$  149.4, 147.3, 143.8, 135.2, 130.6, 129.4, 127.3, 124.9, 123.2 (Ar C), 29.1, 28.2, 26.7, 26.2, 25.3 (CHMe<sub>2</sub>), 21.4 (CMe), 10.7 (AlCH<sub>2</sub>CH<sub>3</sub>), 0.6 (AlCH<sub>2</sub>CH<sub>3</sub>). IR (cm<sup>–1</sup>): 3649 (m), 3258 (s), 3061 (m), 2969 (s), 2869 (s), 2805 (m), 2590 (m), 1917 (m), 1869 (m), 1801 (m), 1701 (m), 1652 (m), 1596 (m), 1494 (m), 1463 (s), 1442 (s), 1383 (m), 1363 (m), 1324 (s), 1290 (s), 1256 (m), 1205 (m), 1183 (m), 1157 (s), 1111 (s), 1093 (m), 1057 (s), 974 (s), 931 (m), 854 (s), 800 (s), 752 (m), 674 (s), 624 (m), 588 (s), 560 (m), 528 (m), 493 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)AlH] (**3**).** To a stirred solution of ArNH(SO<sub>2</sub>-*p*-Tol) (13.24 g, 40.0 mmol) in toluene (100 mL) was added AlH<sub>3</sub>·NMe<sub>3</sub> (2.0 M, 10 mL) in toluene over a period of 30 min. The mixture was stirred at room temperature for an additional 4 h. The resulting solution was concentrated (to ca. 15 mL) and stored at –25 °C overnight to give colorless crystals of **3** (12.41 g, 90%). Mp: 254–255 °C. Anal. Calcd for C<sub>38</sub>H<sub>49</sub>AlN<sub>2</sub>O<sub>4</sub>S<sub>2</sub> (688.29): C, 66.25; H, 7.17; N, 4.07. Found: C, 66.24; H, 6.91; N, 3.86. <sup>1</sup>H NMR (400.15 MHz, CDCl<sub>3</sub>):  $\delta$  7.57 (d, 4H, Ar H), 7.14 (m, 8H, Ar H), 6.86 (d, 2H, Ar H), 4.05 (sept, *J* = 6.80 Hz, 2H, CHMe<sub>2</sub>), 2.81 (sept, *J* = 6.80 Hz, 2H, CHMe<sub>2</sub>), 2.28 (s, 6H, PhMe), 1.41 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>), 1.32 (d, *J* = 6.80 Hz, 6H, CHMe<sub>2</sub>),

(17) Fox examples, see: (a) Hornmiron, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688. (b) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938.

0.97 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 0.26 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.0, 147.1, 144.2, 134.8, 130.0, 129.9, 129.7, 127.7, 127.4, 124.6, 123.3 (Ar C), 28.9, 28.2, 26.0, 25.7, 24.5 ( $\text{CHMe}_2$ ), 21.5 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3257 (s), 3026 (m), 2969 (s), 2927 (s), 2868 (s), 2802 (m), 2713 (m), 2593 (m), 1925 (m), 1865 (m), 1846 (m), 1800 (m), 1699 (m), 1653 (m), 1595 (s), 1495 (m), 1463 (s), 1444 (s), 1398 (m), 1383 (m), 1362 (m), 1323 (s), 1297 (s), 1257 (m), 1210 (m), 1183 (m), 1154 (s), 1112 (s), 1091 (m), 1058 (s), 1020 (m), 976 (m), 917 (m), 863 (s), 800 (s), 705 (m), 673 (s), 633 (m), 587 (m), 561 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)AlI<sub>2</sub>]<sub>2</sub> (4).** A rapidly stirred solution of  $\text{LAlEt}_2$  (4.15 g, 10.0 mmol) in toluene (80 mL) was combined with  $\text{I}_2$  (5.08 g, 20.0 mmol) at room temperature. The deep red solution was stirred for 2 h to give a colorless solution. The solution was concentrated (to ca. 10 mL) and stored at  $-25$  °C overnight to afford white crystals of **4** (5.86 g, 96%). Mp: 226–227 °C. Anal. Calcd for  $\text{C}_{38}\text{H}_{48}\text{Al}_2\text{I}_4\text{N}_2\text{O}_4\text{S}_2$  (1221.98): C, 37.33; H, 3.96; N, 2.29. Found: C, 37.74; H, 4.09; N, 2.31.  $^1\text{H}$  NMR (400.15 MHz, DMSO):  $\delta$  7.60 (d, 4H, Ar H), 7.37 (d, 4H, Ar H), 7.22 (t, 2H, Ar H), 7.09 (d, 4H, Ar H), 3.11 (sept,  $J = 6.80$  Hz, 4H,  $\text{CHMe}_2$ ), 2.34 (s, 6H, Me) 1.44 (d,  $J = 6.80$  Hz, 12H,  $\text{CHMe}_2$ ), 0.92 (d,  $J = 6.80$  Hz, 12H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz, DMSO):  $\delta$  148.3, 142.3, 139.0, 129.9, 129.8, 129.3, 127.9, 126.3, 123.3, (Ar C), 27.8 ( $\text{CHMe}_2$ ), 23.6 (br,  $\text{CHMe}_2$ ), 20.8 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3258 (vs), 2971 (s), 2868 (s), 1925 (m), 1807 (m), 1619 (m), 1597 (m), 1495 (m), 1463 (m), 1398 (m), 1382 (m), 1360 (m), 1323 (s), 1308 (m), 1259 (m), 1182 (m), 1154 (s), 1091 (m), 1052 (m), 917 (m), 796 (s), 670 (s), 611 (m), 560 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)<sub>2</sub>AlI] (5).** **Method A.** A rapidly stirred solution of  $[\text{ArN}(\text{SO}_2\text{-}i\text{-Tol})_2\text{AlEt}]$  (3.59 g, 5.0 mmol) in toluene (40 mL) was combined with  $\text{I}_2$  (1.27 g, 5.0 mmol) at room temperature. The deep red solution was stirred for 3 days to give an orange-red solution. The solution was concentrated (to ca. 10 mL) and stored at  $-25$  °C overnight to afford yellow crystals of **5** (4.07 g, 75%). Mp: 307–308 °C. Anal. Calcd for  $\text{C}_{38}\text{H}_{48}\text{AlIN}_2\text{O}_4\text{S}_2$  (814.19): C, 55.52; H, 5.94; N, 3.44. Found: C, 55.52; H, 6.15; N, 3.14.  $^1\text{H}$  NMR (400.15 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 (d, 4H, Ar H), 7.16 (m, 8H, Ar H), 6.88 (d, 2H, Ar H), 4.03 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 3.03 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 2.29 (s, 6H,  $\text{PhMe}$ ), 1.44 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.32 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 0.95 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 0.19 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.5, 148.4, 145.2, 133.5, 129.9, 129.5, 129.0, 128.1, 124.9, 124.1 (Ar C), 29.5, 28.5, 28.4, 26.3, 25.3 ( $\text{CHMe}_2$ ), 21.8 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3260 (s), 3059 (s), 2970 (s), 2868 (s), 2591 (m), 1916 (m), 1873 (m), 1800 (m), 1699 (m), 1650 (m), 1595 (s), 1558 (m), 1494 (m), 1463 (s), 1441 (s), 1384 (m), 1363 (m), 1325 (s), 1296 (s), 1255 (m), 1206 (s), 1183 (m), 1158 (s), 1108 (s), 1047 (s), 1032 (s), 972 (s), 932 (m), 861 (s), 802 (s), 753 (m), 720 (m), 704 (m), 676 (s), 597 (s), 561 (m), 515 (m), 443 (m), 411 (m).

**Method B.** A solution of  $\text{LAlI}_2$  (0.61 g, 1.0 mmol) in diethyl ether (40 mL) was added to a suspension of  $\text{KC}_8$ , which was freshly prepared from graphite and potassium (0.08, 2.0 mmol) in diethyl ether (10 mL). The mixture was stirred at room temperature for 24 h. It was filtered, and the yellow filtrate was concentrated (to ca. 5 mL) and stored at  $-25$  °C overnight to yield yellow crystals of **5** (0.31 g, 46%).

**[ArN(SO<sub>2</sub>-*p*-Tol)<sub>2</sub>AlNHP] (6).** To a stirred solution of  $\text{L}_2\text{AlH}$  (3.44 g, 5.0 mmol) in toluene (50 mL) was added  $\text{PhNH}_2$  (0.46 mL, 5.0 mmol). The solution was refluxed for 2 h and then cooled to room temperature and concentrated (ca. 10 mL). The solution was stored at  $-25$  °C overnight to afford colorless crystals of **6** (3.28 g, 84%). Mp: 164 °C dec. Anal. Calcd for  $\text{C}_{44}\text{H}_{54}\text{AlN}_3\text{O}_4\text{S}_2$  (779.34): C, 67.75; H, 6.98; N, 5.39. Found: C, 67.67; H, 6.82; N, 5.39.  $^1\text{H}$  NMR (400.15 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.51 (d, 4H, Ar H), 7.20 (d, 2H, Ar H), 7.15 (m, 4H, Ar H), 6.96 (d, 4H, Ar H), 6.85 (d, 2H, Ar H), 6.78 (d, 2H, Ar H), 6.63 (t, 1H, Ar H), 4.11 (sept,

$J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 3.57 (s, 1H, NH), 3.11 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 2.20 (s, 6H,  $\text{PhMe}$ ), 1.45 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.34 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.00 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 0.00 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.5, 149.4, 147.7, 144.3, 134.1, 129.8, 129.6, 129.3, 128.7, 127.4, 124.8, 123.8, 117.8, 116.1 (Ar C), 29.1, 27.7, 26.6, 26.1, 25.2, 22.7 ( $\text{CHMe}_2$ ), 21.4 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3832 (m), 3600 (m), 3511 (m), 3440 (m), 3250 (s), 2971 (s), 2867 (s), 1930 (m), 1596 (m), 1499 (m), 1467 (m), 1444 (m), 1401 (m), 1324 (s), 1254 (m), 1185 (m), 1153 (s), 1089 (m), 1049 (m), 916 (m), 794 (m), 750 (m), 666 (s), 612 (m), 559 (s), 477 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)<sub>2</sub>AlCCPh] (7).** To a stirred solution of **3** (3.44 g, 5.0 mmol) in toluene (80 mL) was added phenylacetylene (0.55 mL, 5.0 mmol). The solution was refluxed for 10 h and then cooled to room temperature. The solution was concentrated (to ca. 20 mL) and cooled to  $-25$  °C to give colorless crystals of **7** (2.55 g, 65%). Mp: 142 °C dec. Anal. Calcd for  $\text{C}_{46}\text{H}_{53}\text{AlN}_2\text{O}_4\text{S}_2$  (788.33): C, 70.02; H, 6.77; N, 3.55. Found: C, 70.43; H, 6.55; N, 3.49.  $^1\text{H}$  NMR (400.15 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.88 (d, 4H, Ar H), 7.47 (d, 2H, Ar H), 7.33 (m, 3H, Ar H), 7.18 (t, 2H, Ar H), 7.12 (m, 6H, Ar H), 6.88 (d, 2H, Ar H), 4.06 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 3.19 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 2.28 (s, 6H,  $\text{PhMe}$ ), 1.43 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.33 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.04 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 0.26 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.1, 147.8, 144.3, 134.5, 131.6, 129.7, 129.5, 128.6, 128.4, 127.8, 127.5, 125.1, 124.5, 123.5, 109.8 (AlC), 106.5 (CPh), 29.0, 28.2, 26.8, 25.8, 24.7, 21.8 ( $\text{CHMe}_2$ ), 21.5 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3257 (s), 2972 (s), 2870 (m), 2798 (m), 2579 (m), 2353 (m), 2102 (m), 2025 (m), 1930 (m), 1661 (m), 1595 (m), 1456 (s), 1401 (s), 1320 (m), 1258 (m), 1213 (m), 1155 (s), 1093 (s), 1051 (s), 980 (m), 915 (m), 863 (m), 805 (m), 753 (m), 669 (s), 604 (m), 552 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)<sub>2</sub>AlOCHPh<sub>2</sub>] (8).** To a stirred solution of **3** (1.38 g, 2.0 mmol) in toluene (40 mL) was added benzophenone (0.36 g, 2 mmol). The solution was refluxed for 6 h and then cooled to room temperature. The solution was concentrated (to ca. 10 mL) and stored at  $-25$  °C overnight to yield colorless crystals of **8** (0.91 g, 52%). Mp: 112 °C dec. Anal. Calcd for  $\text{C}_{51}\text{H}_{59}\text{AlN}_2\text{O}_5\text{S}_2$  (870.37): C, 70.32; H, 6.83; N, 3.22. Found: C, 69.90; H, 6.60; N, 3.21.  $^1\text{H}$  NMR (400.15 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.66 (d, 2H, Ar H), 7.45 (d, 2H, Ar H), 7.33 (m, 8H, Ar H), 7.08 (d, 6H, Ar H), 6.88 (d, 4H, Ar H), 6.59 (d, 2H, Ar H), 6.32 (s, 1H,  $\text{CHPh}_2$ ), 4.09 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 3.15 (sept,  $J = 6.80$  Hz, 2H,  $\text{CHMe}_2$ ), 2.13 (s, 6H,  $\text{PhMe}$ ), 1.44 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ), 1.28 (t,  $J = 7.60$  Hz, 12H,  $\text{CHMe}_2$ ), 0.04 (d,  $J = 6.80$  Hz, 6H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.5, 148.0, 147.5, 143.7, 137.9, 133.8, 130.0, 129.5, 129.4, 129.0, 128.7, 128.4, 128.2, 127.4, 127.0, 126.5, 125.8, 125.3, 124.9, 123.7, 109.7 ( $\text{CHPh}_2$ ), 29.2, 27.7, 27.2, 26.4, 25.2, 22.1 ( $\text{CHMe}_2$ ), 21.4 ( $\text{CMe}$ ). IR ( $\text{cm}^{-1}$ ): 3260 (s), 3063 (m), 3027 (m), 2975 (s), 2867 (m), 1804 (m), 1656 (m), 1595 (m), 1495 (m), 1453 (s), 1397 (m), 1324 (s), 1288 (s), 1252 (m), 1203 (m), 1152 (s), 1054 (s), 974 (m), 917 (m), 862 (s), 796 (s), 739 (m), 668 (s), 696 (m), 559 (m).

**[ArN(SO<sub>2</sub>-*p*-Tol)Li(THF)<sub>2</sub>] (9).** To a stirred solution of  $\text{ArNH}(\text{SO}_2\text{-}i\text{-Tol})$  (1.66 g, 5.0 mmol) in toluene (40 mL) was added  $n\text{-BuLi}$  (2.5 M, 2 mL) in  $n\text{-hexane}$ . The mixture was stirred at room temperature for 24 h, during which time a white solid was formed. The solid was isolated by filtration and crystallized from THF at  $-25$  °C to give colorless crystals of **9** (1.23 g, 52%). Mp: 330–332 °C. Anal. Calcd for  $\text{C}_{54}\text{H}_{80}\text{Li}_2\text{N}_2\text{O}_8\text{S}_2$  (962.57): C, 67.33; H, 8.37; N, 2.91. Found: C, 67.09; H, 8.37; N, 3.03.  $^1\text{H}$  NMR (400.15 MHz, DMSO):  $\delta$  7.41 (d, 4H, Ar H), 7.05 (d, 4H, Ar H), 6.76 (d, 4H, Ar H), 6.64 (t, 2H, Ar H), 3.60 ( $J = 6.40$  Hz, 8H,  $\text{OCH}_2\text{CH}_2$ ), 3.51 (sept.,  $J = 6.80$  Hz, 4H,  $\text{CHMe}_2$ ), 2.27 (s, 6H,  $\text{PhMe}$ ) 1.76 (m, 8H,  $\text{OCH}_2\text{CH}_2$ ), 0.84 (d,  $J = 6.80$  Hz, 24H,  $\text{CHMe}_2$ ).  $^{13}\text{C}$  NMR (100.63 MHz, DMSO):  $\delta$  147.9, 144.7, 144.0, 136.6, 127.6, 125.3, 121.6, 119.7 (Ar C), 66.97 ( $\text{OCH}_2\text{CH}_2$ ), 27.0 ( $\text{CHMe}_2$ ), 25.1

(CHMe<sub>2</sub>), 24.0 (OCH<sub>2</sub>CH<sub>2</sub>), 20.8 (CMe). IR (cm<sup>-1</sup>): 2864 (s), 1495 (m), 1465 (m), 1436 (s), 1380 (m), 1321 (s), 1257(m), 1209(m), 1116 (s), 1084 (s), 990 (s), 819 (m), 784 (m), 568 (m).

**Polymerization Procedure.** Lactide polymerizations were carried out by charging a Schlenk flask with *rac*-lactide (1.44 g) and toluene (20 mL) with the appropriate amount of catalysts. The flask was immediately immersed in an oil bath at 125 °C. After an appropriate time, the oil bath was removed, and all volatiles were removed. The remaining solid was dissolved in a small amount of THF, and then water was added to incipient precipitation. The precipitated polymers were collected, washed with water twice, and dried under vacuum for 24 h. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of PLA samples were recorded in CDCl<sub>3</sub>.

**X-ray Structural Determination.** All intensity data were collected with a Bruker SMART CCD diffractometer, using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were resolved by direct methods and refined by full-

matrix least squares on  $F^2$ . Hydrogen atoms were considered in calculated positions. All non-hydrogen atoms were refined anisotropically. Crystal data and data collection details are collected in Tables 1 and 2. Crystals of **1–4**, **7** and **8** suitable for X-ray analysis were obtained from toluene at room temperature, and those of **9** were obtained from THF at room temperature.

**Acknowledgment.** This work was supported by the Program for New Century Excellent Talents in Universities (the NCET) and Tianjin Natural Science Foundation.

**Supporting Information Available:** CIF files for compounds **1–4**, and **7–9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0611296