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Neutral and Cationic Aluminum Complexes Supported by Acetamidate and Thioacetamidate Heteroscorpionate Ligands as Initiators for Ring-Opening Polymerization of Cyclic Esters

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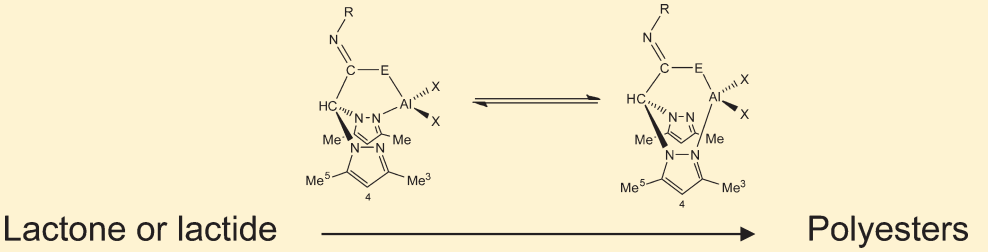
Supporting Information

ABSTRACT:



The synthesis, structures, and ring-opening polymerization (ROP) activity of heteroscorpionate aluminum alkyl and aryloxide complexes are reported. The reactions of the acetamide and thioacetamide heteroscorpionate protio ligands pbptamH (pbptamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide), pbpamH (pbpamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)-acetamide), sbpamH (sbpamH = *N*-*sec*-butyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide), and (*S*)-mbpamH ((*S*)-mbpamH = (*S*)-(−)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide) with 1 equiv of AlR_3 (R = Me, Et, ^{i}Bu) proceed in very high yields to give the neutral heteroscorpionate dialkyl aluminum complexes $[AlR_2\{\kappa^2\text{-pbptam}\}]$ (R = Me (**1**), Et (**2**)), $[AlR_2\{\kappa^2\text{-pbptam}\}]$ (R = Me (**3**), Et (**4**), ^{i}Bu (**5**)), $[AlR_2\{\kappa^2\text{-pbptam}\}]$ (R = Me (**6**), Et (**7**), ^{i}Bu (**8**)), and $[AlR_2\{\kappa^2\text{-(}S\text{)-mbpam}\}]$ (R = Me (**9**), Et (**10**)). In the solid state, complexes **1**−**10** adopt a tetrahedral structure with the heteroscorpionate ligands arranged in a κ^2 coordination mode; in the case of the thioacetamidate derivatives **1** and **2** a κ^2NN coordination mode is observed, whereas the acetamidate derivatives **3**−**10** present a κ^2NO coordination mode. The structures in solution of **1**−**10** were investigated by VT NMR spectroscopy, and fluxional exchange between coordinated and noncoordinated pyrazole rings was observed, producing interconversion between the different isomers. Compounds **7** and **10** were used as convenient starting materials for the synthesis of the aryloxide aluminum compounds $[Al(OR)_2\{\kappa^2\text{-sbpam}\}]$ (**11**) and $[Al(OR)_2\{\kappa^2\text{-(}S\text{)-mbpam}\}]$ (**12**) (R = 2,6-$Me_2C_6H_3O$) by reaction with the corresponding 2,6-dimethylphenol. The complexes $[AlMe\{\kappa^3\text{-pbptam}\}][MeB(C_6F_5)_3]$ (**13**), $[AlMe\{\kappa^3\text{-pbptam}\}][B(C_6F_5)_4]$ (**14**), $[AlEt\{\kappa^3\text{-pbptam}\}][B(C_6F_5)_4]$ (**15**), $[AlEt\{\kappa^3\text{-sbpam}\}][B(C_6F_5)_4]$ (**16**), and $[AlEt\{\kappa^3\text{-(}S\text{)-mbpam}\}][B(C_6F_5)_4]$ (**17**) are derived from the ionization of the neutral dialkyl aluminum complexes **1**, **2**, **7**, and **10** with the alkyl abstracting reagent $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$. The NMR data were consistent with an overall C_s-symmetric structure for **13**−**15** and C_1-symmetric structure for **16** and **17**, which indicates an effective κ^3 coordination of the corresponding heteroscorpionate ligand to the cationic aluminum center. The structures of the complexes were determined by spectroscopic methods, and the X-ray crystal structures of **1**, **2**, and **7** were also established. Finally, exhaustive comparative catalytic studies of the aluminum complexes **1**−**10**, **13**, and **14** in the ring-opening polymerization of *rac*-lactide, L-lactide, and ε-caprolactone are also described.

INTRODUCTION

Ecologically acceptable complements to saturated polyolefins—the consumption of which has risen steadily since the spectacular discovery of alkene polymerization—include biodegradable polymers such as polylactides and polylactones.[1,2] The scientific interest in well-defined polymer architectures results from the need to obtain polymers with good mechanical properties. In order to achieve this goal, the microstructure of the polymeric chains, including their molecular weight and polydispersity, needs to be controlled and this can be performed using catalysis. In this context, interest in the past decade in the catalytic

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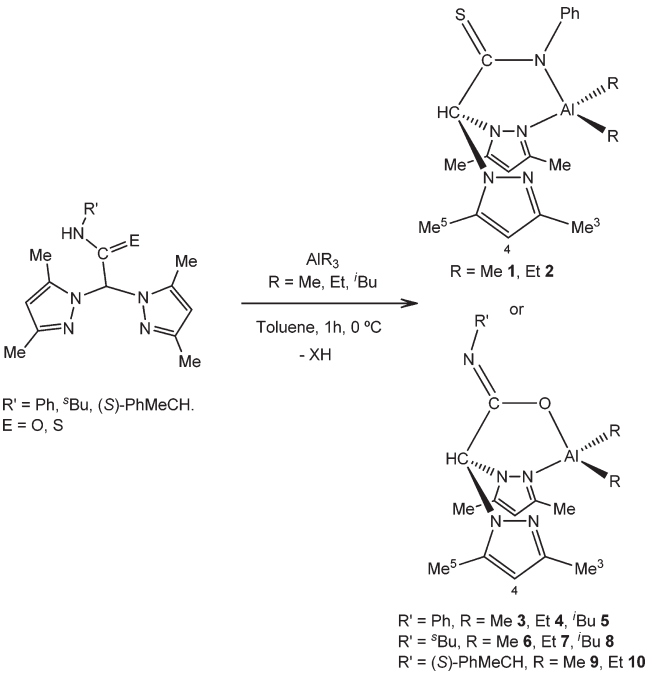
ring-opening polymerization (ROP) of lactones and lactides has spurred several review articles.[3] Numerous single-site catalysts bearing electrophilic metal ions, such as magnesium,[4] calcium,[4,5] titanium,[6] lanthanide,[7] iron,[8] zinc,[9] tin,[10] and aluminum,[11] are well-known. Aluminum complexes are among the most efficient catalysts for lactone and lactide polymerizations and are generally established using N- and/or O-supported ligands. Among the variety of catalysts, many chiral aluminum alkoxides supported by tetradentate Schiff base ligands have been highlighted as highly selective in the polymerization of *rac*-lactide or *meso*-lactide.[11c,e,g−i,k] The nature of the ancillary ligand in the aluminum coordination sphere is an obvious key parameter that determines the steric and electronic properties and, in turn, the catalytic performances of these complexes. As a result, there is an ongoing search for such new ancillaries. Heteroscorpionate ligands represent one of the most versatile types of anionic tridentate ligands that can coordinate to a variety of elements, e.g., from transition metals to main-group metals.[12] In recent years, chemistry based on the design of this particular type of intriguing heteroscorpionate ligand has been extended considerably in terms of coordination chemistry[13] and catalytic applications.[14] In the past decade a number of research groups have contributed widely to this field, designing new heteroscorpionate ligands related to the bis(pyrazol-1-yl)methane system and incorporating several pendant donor arms bearing an anionic functional donor group, such as carboxylate, dithiocarboxylate, aryloxide, alkoxide, amide, cyclopentadienyl, acetamidate, thioacetamidate, and amidinate.[15] Furthermore, some of these ligands have been designed as chiral ligands with high enantiopurity, which is an important goal in organometallic chemistry in order to prepare metal-based reagents through efficient stereochemical control in asymmetric processes.[16] In this field, our research group and others are interested in extending the scope of this chemistry to the synthesis of heteroscorpionate complexes of the main-group metals, such as lithium, magnesium, calcium, and aluminum,[17] the chemistry of which in terms of scorpionate ligands is based mainly on Trofimenko's borate ($Tp^{RR'}$) ligands.[18] Some of these scorpionate and heteroscorpionate aluminum complexes are active initiators in the ring-opening polymerization of cyclic esters. We have already focused on the possibility of designing organoaluminum entities in order to study their synthetic accessibility, structural arrangements, and catalytic behavior in the ring-opening polymerization of polar monomers such as ε-caprolactone and lactide. We previously reported the first aluminum complexes with thioacetamidate heteroscorpionate ligands, and these exhibit high versatility in terms of coordination modes due to the existence of three possible tautomers.[19] Bearing in mind the potential applications of the element aluminun in catalysis, it was of interest to prepare new neutral and cationic scorpionate aluminum complexes with potential as high-activity initiators for cyclic ester polymerization. Herein, we describe in detail the synthesis and characterization of a series of chiral heteroscorpionate alkyl and aryloxide aluminum complexes, including cationic derivatives and some enantiopure complexes. The performance of these complexes in the polymerization of ε-caprolactone and L-/*rac*-lactide was explored under well-controlled conditions.

Scheme 1. Summary of Reactions Leading to Complexes 1−10



RESULTS AND DISCUSSION

Syntheses and Structural Characterization. Acetamide or thioacetamide heteroscorpionate precursors contain Lewis basic coordinating groups (N and O or S centers in the "arm" of the heteroscorpionate moiety), and this makes them an interesting type of ligand for the preparation of aluminum complexes, due to their wide variety of coordination modes.[20] We previously observed that thioacetamide ligands, which contain both hard and soft donor atoms, bond to the hard Lewis acid Al(III) by the hard donor atom (N) of the thioacetamidate moiety.[19] Bearing this information in mind, we reacted the corresponding trialkylaluminum with the protonated acetamide or thioacetamide heteroscorpionate precursors[20] pbptamH (pbptamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide), pbpamH (pbpamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide), sbpamH (sbpamH = *N*-*sec*-butyl-2,2-bis(3,5-dimethylpyrazol-1-yl)-acetamide), and (*S*)-mbpamH ((*S*)-mbpamH = (*S*)-(−)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide) in a 1:1 molar ratio in toluene at 0 °C. These reactions gave the mononuclear dialkyl aluminum complexes $[AlR_2\{\kappa^2\text{-pbptam}\}]$ (R = Me (**1**), Et (**2**)), $[AlR_2\{\kappa^2\text{-pbpam}\}]$ (R = Me (**3**), Et (**4**), ^{i}Bu (**5**)), $[AlR_2\{\kappa^2\text{-sbpam}\}]$ (R = Me (**6**), Et (**7**), ^{i}Bu (**8**)) and $[AlR_2\{\kappa^2\text{-}(S)\text{-mbpam}\}]$ (R = Me (**9**), Et (**10**)) with vigorous elimination of the corresponding alkane (Scheme 1). Compounds **1** and **2** were isolated as yellow solids, and compounds **3**−**10** were isolated as white solids, all in good yields, after the appropriate workup procedure. All of the complexes were isolated as chiral compounds, and **9** and **10** were obtained as enantiopure compounds.

The ^{13}C NMR signals of the carbonyl and thiocarbonyl groups in these complexes have been good indicators of the bonding mode of acetamidate or thioacetamidate moieties of the ligands. The acetamidate carbon resonance, RNCO, is shifted to higher field with respect to that of neutral ligands[20a] (see the Experimental Section), indicating that the acetamidate moiety is coordinated to the aluminum center through the O atom (see Scheme 1). In contrast, the corresponding signal for the thioacetamidate carbon resonance, RNCS, is shifted to lower field with respect to that in the neutral ligand[20a] (see the Experimental

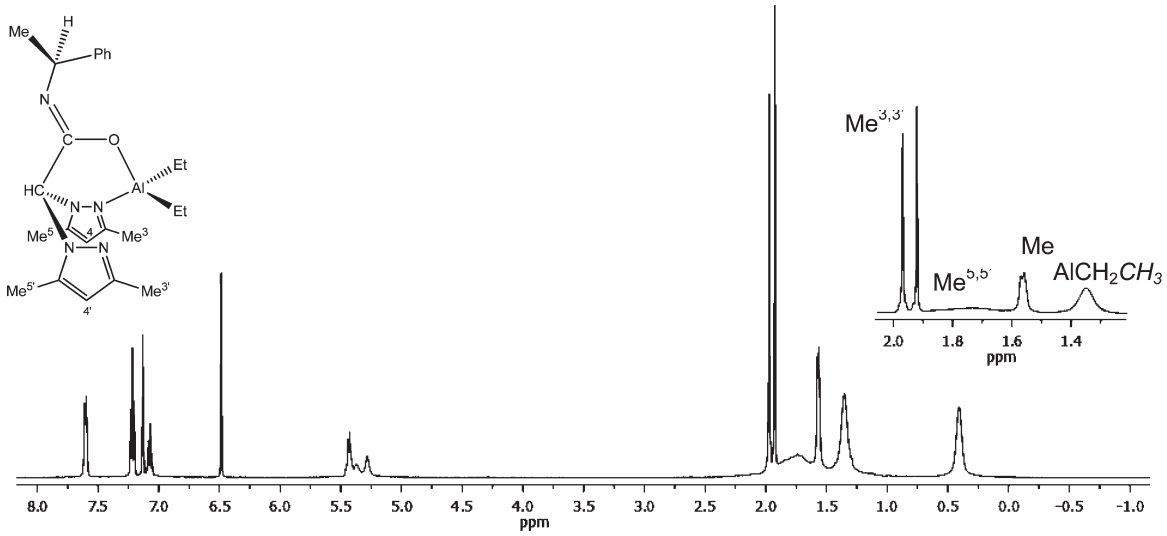
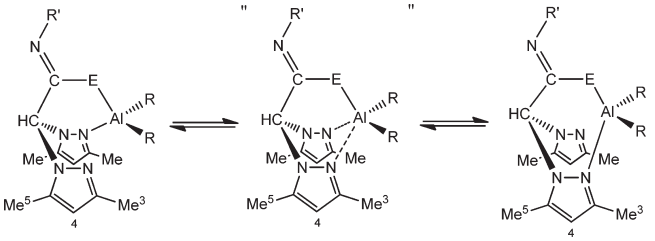


Figure 1. ^{1}H NMR spectrum of [AlEt$_2${κ^2-(*S*)-mbpam}] (**10**).

Scheme 2



Section), indicating that the thioacetamidate moiety is coordinated to the metal center through the N atom (see Scheme 1). However, a small amount of delocalized E−C−N bond probably exists in the acetamidate or thioacetamidate moieties of the heteroscorpionate ligands.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1**−**5** (without a chiral carbon) at room temperature show a singlet for each of the H^4, Me^3, and Me^5 pyrazole protons and carbons, indicating that the pyrazoles are equivalent, along with one resonance for the two equivalent alkyl ligands. It is worth noting that some pyrazole proton signals appear as broad resonances, a finding that indicates fluxional behavior (Scheme 2), which is thought to be due to an exchange process between a coordinated and a noncoordinated pyrazole ring (see discussion below). Furthermore, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **6**−**10** (which do contain a stereogenic carbon) show two singlets for each of the H^4, Me^3, and Me^5 pyrazole protons and carbons, some of them as broad resonances (see Figure 1). Moreover, the signals of the alkyl groups at the aluminum center appear as a single broad resonance. These data also confirm the presence of an exchange process between the coordinated and the noncoordinated pyrazole rings (Scheme 2).

NOESY-1D NMR experiments permitted the unequivocal assignment most of the ^{1}H NMR resonances. The response in the ^{1}H NOESY-1D experiment from the ortho protons of the phenyl ring from the thioacetamidate moiety on irradiating each of the alkyl groups suggests coordination by the N atom of the thioacetamidate moiety in compounds **1** and **2**. However, similar irradiation in compounds **3**−**10** did not lead to any enhancement of the N−R group. ^{1}H−^{13}C heteronuclear correlation (g-HSQC) experiments were carried out, and these allowed us to assign the resonances corresponding to C^4, Me^3, and Me^5 of the pyrazole rings and alkyl groups. The data support a tetrahedral disposition for the aluminum atom with a κ^2NN coordination mode of the thioacetamidate heteroscorpionate ligand, whereas the acetamidate derivatives have a κ^2NO coordination mode, as depicted in Scheme 1.

Two examples of variable-temperature NMR studies are discussed below for complexes with an achiral and a chiral heteroscorpionate ligand, respectively. In the case of complex **2** the VT NMR analysis showed that the resonances of the ethyl groups directly bonded to the aluminum center, as well as those of the pyrazole rings, broaden and become resolved into two separate peaks at −70 °C. A stacked plot of the relevant sections of the variable-temperature ^{1}H NMR spectra of **2** is shown in Figure 2. At room temperature the exchange is too fast to be detected on the NMR time scale and the two pyrazole rings therefore appear equivalent. Thus, an exchange process between a coordinated and noncoordinated pyrazole ring is taking place and this involves interconversion from one stereoisomer to the other. It is worth noting that, given the coordination mode of the ligands, all the complexes are chiral compounds regardless of the existence of a chiral center in the heteroscorpionate ligand used as the scaffold.

The variable-temperature NMR study for complex **6** provides a good example of a compound bearing a chiral heteroscorpionate ligand. In the ^{1}H NMR spectra shown in Figure 3 signals can be observed for the CH, H^4, H$^{4'}$, and CH* protons of the heteroscorpionate ligand at room temperature. When the temperature was decreased to below −80 °C, two signals (relative intensities 2:1) were observed for each of the diastereoisomers present (see Scheme 3). For complexes **6**−**8**, which contain a racemic heteroscorpionate ligand, there are four stereoisomers, while for complexes **9** and **10**, which contain an enantiopure heteroscorpionate ligand, there are only two diastereoisomers.

The VT NMR analyses carried out on complexes **1**−**10** (from +40 to −80 °C) allowed us to evaluate a series of kinetic parameters. The rate constants k_{ex} at each temperature were

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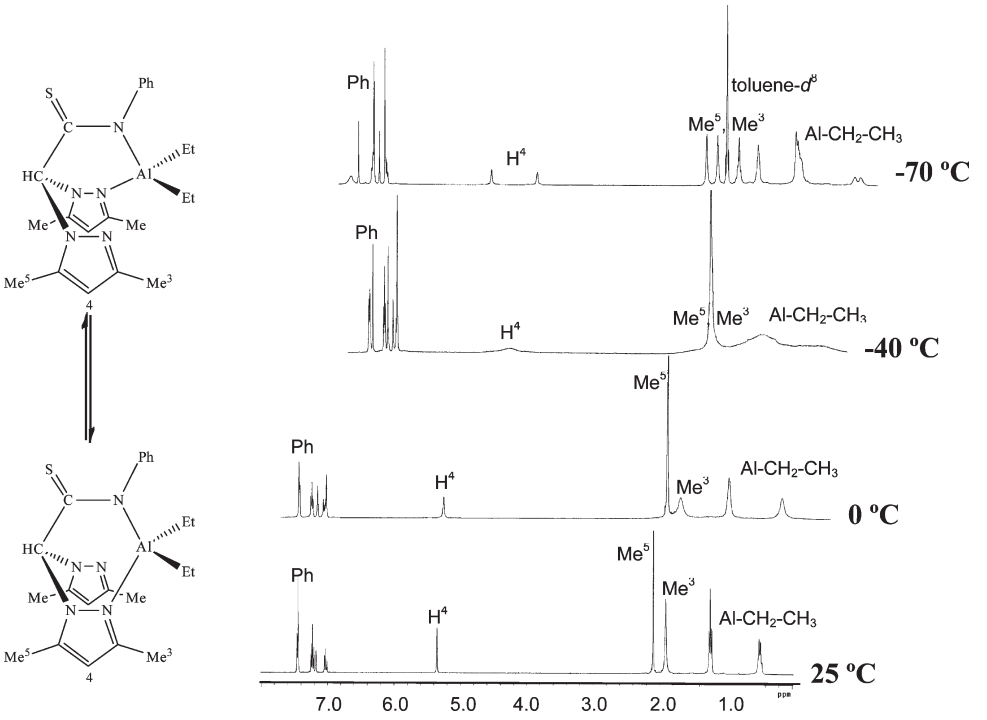

Figure 2. Variable-temperature ^{1}H NMR spectra of compound **2** in toluene-d_8.

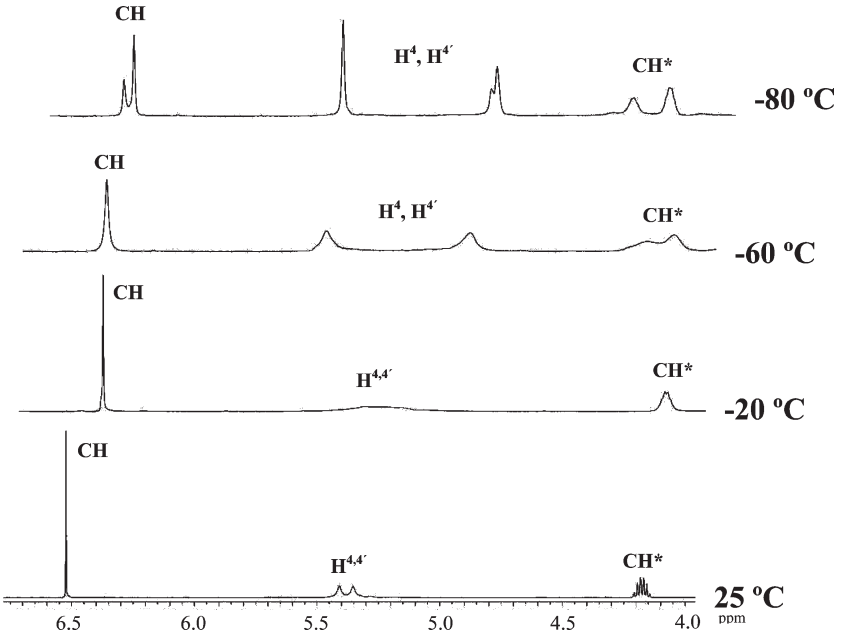

Figure 3. Variable-temperature ^{1}H NMR spectra in the region from 6.5 to 4.0 ppm for compound **6**.

estimated by visual matching of line shapes of simulated and experimental spectra for complexes **1**−**10** (see Table 1).[21] The activation enthalpies, activation entropies, and Gibbs free energies at 20 °C were evaluated from the Eyring plot (see Figures S1−S9 in the Supporting Information).[21]

The data collected in Table 1 allow several trends to be highlighted. Compound **1** has the lowest activation barrier, and at −80 °C it is close to the coalescence point, which precluded an evaluation of the kinetic parameters for this compound. Furthermore, it can be observed that aluminum compounds **1**, **3**, and **9** (bearing a methyl ligand) show the fastest site exchange by a significant margin, while complexes **5** and **8** (bearing an isobutyl ligand) exhibit the slowest site exchange (see the rate constant k_{ex} values in Table 1). It is clear that the replacement of the methyl or ethyl ligand by the bulkier isobutyl ligand leads to a significant deceleration of k_{ex} in the compounds, evidently the result of increasing steric hindrance on the aluminum with the bulkiness of the substituents (see Figure S10 in the Supporting

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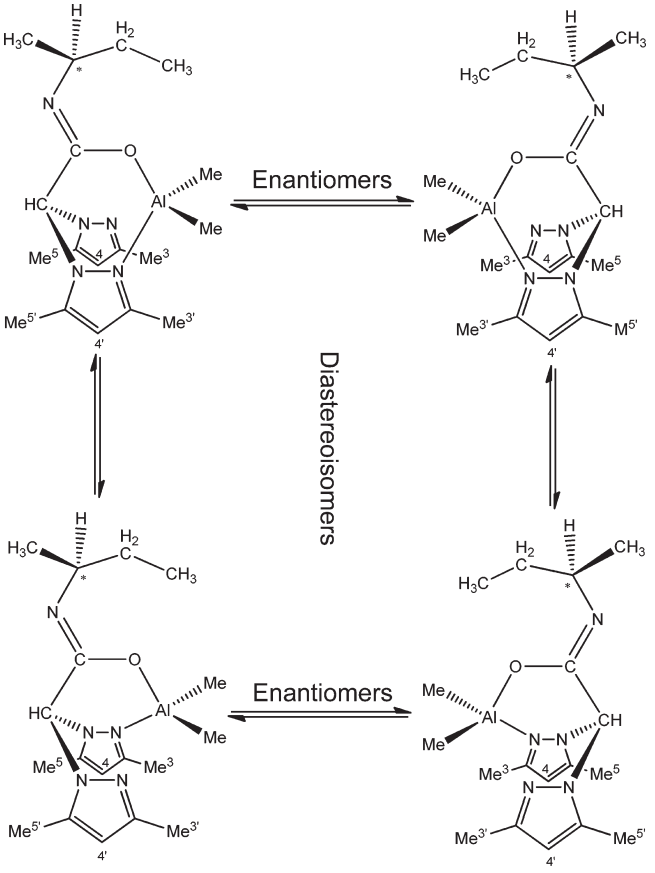
Information). Additionally, the increase in the activation enthalpy and the slight variation in the activation entropy on increasing the bulk of the alkyl substituent support an intramolecular associative displacement mechanism in which the pyrazole ring that is outside the coordination sphere of the metal center displaces the coordinated pyrazole ring through a pentacoordinate transition state. The approach of the free pyrazole ring is necessarily from the opposite side of the coordinated pyrazole ring; therefore, inversion of configuration at the metal center occurs (see Scheme 2). A similar exchange mechanism for coordinated and uncoordinated pyrazole groups was previously observed in tris(pyrazol-1-yl)hydroborato and other heteroscorpionate aluminum complexes.[17g,18d,18f]

Scheme 3. Proposed Structures for the Four Enantiomers of Compound 6



The molecular structures of complexes **1**, **2**, and **7** were determined by X-ray diffraction. The corresponding ORTEP drawings are depicted in Figure 4. In all cases, the heteroscorpionate ligand is κ^2 coordinated to Al, κ^2NN for thioacetamidate complexes and κ^2NO coordinated for the acetamidate complex, forming pseudotetrahedral complexes with C_1 symmetry. The crystallographic data are given in Table S1 (Supporting Information), and selected interatomic distances and angles are given in Table 2. The solid-state structures are consistent with those proposed in Scheme 1 on the basis of solution NMR and other analytical data. Given the coordination mode of the heteroscorpionate ligand, complexes **1**, **2**, and **7** are chiral compounds. These complexes crystallize as a racemic mixture with both enantiomers included in the unit cells, which belong to centrosymmetric space groups. The geometry around the Al center can be described for all complexes as distorted tetrahedral, with the dihedral angle between the N1−Al−E and C−Al−C planes (89.2, 85.7, and 85.22° for **1**, **2**, and **7**, respectively) consistent with a tetrahedral geometry. Furthermore, the angles around the Al atom show considerable deviation from ideal values (range 92.7(4)−116.1(4)° for **1**, 92.5(4)−116.9(4)° for **2**, 94.6(2)−119.1(8)° for **7**), and in all compounds the most acute angle of 92.7(4)° for **1**, 92.5(4)° for **2**, and 94.6(2)° for **7** is observed for N1−Al−E, which is constrained by the bite of the heteroscorpionate ligand. The distances between N(4) or N(3) and Al of 3.34(1) Å for **1**, 3.298(4) Å for **2**, and 3.434(5) Å for **7** are too long to be considered as bonding or an interaction between N(4) or N(3) and the Al atom, probably due to the steric hindrance caused by the two alkyl groups. The Al−C distances (range 1.953(5)−2.00(3) Å) are in good agreement with literature data.[17f,g,18,19] The Al−N1 bond distances of 1.941(9) Å for **1**, 1.935 (4) Å for **2**, and 1.953(5) Å for **7** are similar to those in Al/pyrazolyl complexes.[17f,g,18,19] The bond distance of 1.775(4) Å for Al−O1 of **7** is shorter than the Al−N5 distances of 1.932(9) and 1.918(4) Å for **1** and **2**, respectively.

It was envisaged that the new aluminum alkyls would serve as starting materials to prepare the corresponding alkoxide complexes, which are usually better initiators for ROP. Unfortunately, reaction of **1**−**10** with either isopropyl or ethyl alcohol yielded mixtures of protio ligand, residual metal alkyl, and $Al(OR)_3$ species in toluene at room temperature; in alternative solvents and/or at high dilution the reactions gave similar mixtures. Thus, evidence for the formation of alkoxide aluminum species was not observed. While the reaction of the alkyl organoaluminums **1**−**10** with 1 or 2 equiv of a source of aliphatic alcohol consistently yielded intractable mixtures, the reaction of **7** and **10** with 2 equiv

Table 1. Summary of Kinetic Parameters for the Isomerization of Compounds 1−10

complex	$T_{coalescence}$ (°C)	k_{ex}(20 °C) (s^{-1})	$\Delta G^{\ddagger}$(20 °C) (kcal mol^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
1	−90	n.d.	n.d.	n.d.	n.d.
2	−40	8300 ± 200	7.1 ± 0.1	7.4 ± 0.5	−24.2 ± 2.5
3	−50	8900 ± 200	3.5 ± 0.1	11.0 ± 0.7	−11.8 ± 2.7
4	−20	4100 ± 150	3.8 ± 0.1	11.8 ± 0.6	−12.9 ± 2.6
5	30	350 ± 20	4.1 ± 0.1	12.4 ± 0.7	−13.8 ± 2.7
6	−20	4300 ± 150	8.4 ± 0.1	6.8 ± 0.9	−28.6 ± 3.8
7	0	1800 ± 80	8.8 ± 0.1	7.0 ± 0.8	−30.0 ± 3.2
8	30	80 ± 10	9.7 ± 0.5	7.5 ± 0.6	−33.0 ± 2.2
9	−40	9200 ± 200	5.2 ± 0.1	9.0 ± 0.7	−17.8 ± 3.0
10	−10	6100 ± 100	5.4 ± 0.2	9.8 ± 0.8	−18.3 ± 3.6

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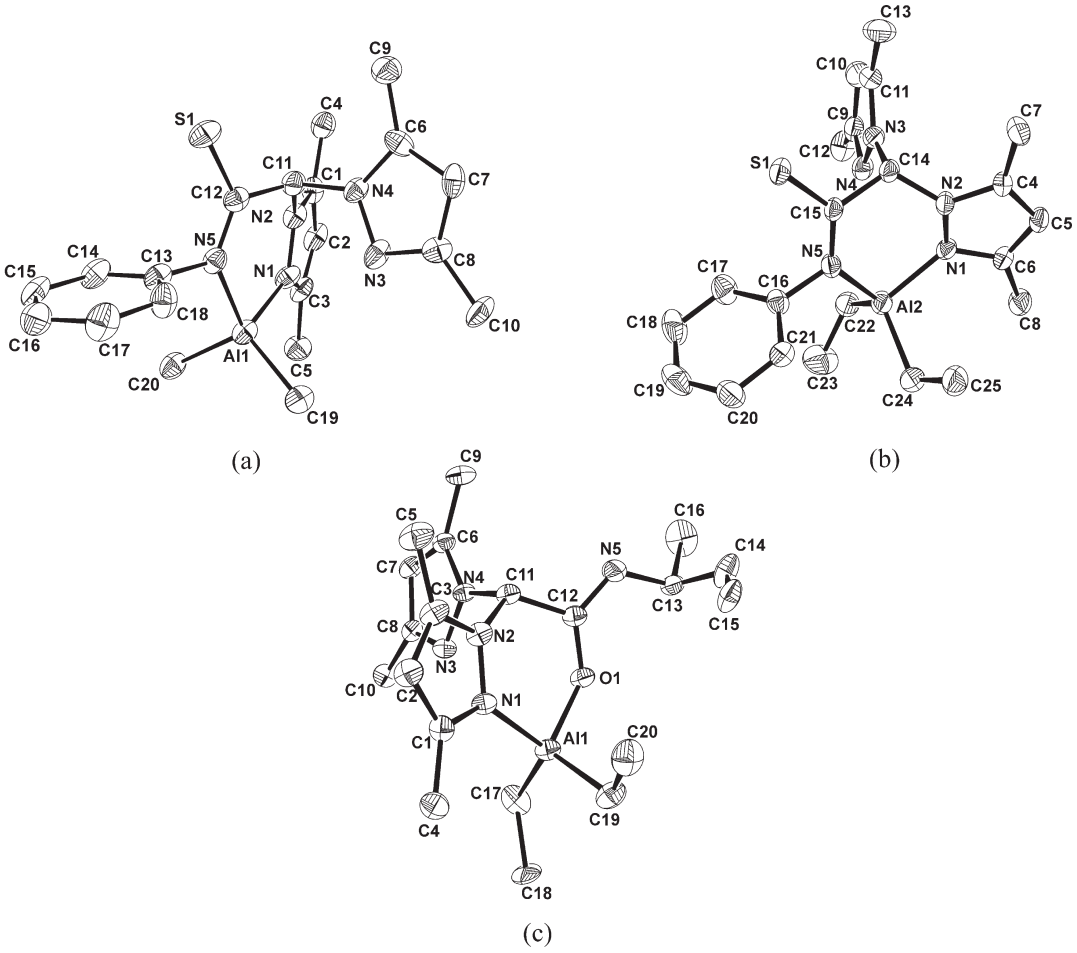

Figure 4. ORTEP drawings of compounds **1** (a), **2** (b), and **7** (c). Thermal ellipsoids are set at the 30% probability level, and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 2, and 7

1							
molecule 1		molecule 2		2		7	
Al(1)−N(1)	1.941(9)	Al(2)−N(6)	1.93(1)	N(1)−Al(2)	1.935(4)	Al(1)−N(1)	1.953(5)
Al(1)−N(5)	1.932(9)	Al(2)−N(10)	1.929(8)	N(5)−Al(2)	1.918(4)	Al(1)−O(1)	1.775(4)
Al(1)−C(19)	1.97(1)	Al(2)−C(40)	1.96(1)	C(22)−Al(2)	1.953(5)	Al(1)−C(19)	1.962(6)
Al(1)−C(20)	1.98(1)	Al(2)−C(41)	1.97(1)	C(24)−Al(2)	1.971(5)	Al(1)−C(17)	2.00(3)
S(1)−C(12)	1.69(1)	S(2)−C(32)	1.68(1)	C(15)−S(1)	1.672(4)	O(1)−C(12)	1.318(6)
C(11)−C(12)	1.51(1)	C(31)−C(32)	1.55(1)	C(14)−C(15)	1.537(5)	C(11)−C(12)	1.517(7)
N(5)−C(12)	1.32(1)	N(10)−C(32)	1.30(1)	C(15)−N(5)	1.332(5)	N(5)−C(12)	1.273(7)
N(5)−C(13)	1.42(1)	N(10)−C(33)	1.45(1)	C(16)−N(5)	1.444(5)	N(5)−C(13)	1.51(2)
N(5)−Al(1)−N(1)	92.7(4)	N(10)−Al(2)−N(6)	92.5(4)	N(5)−Al(2)−N(1)	94.8(1)	O(1)−Al(1)−N(1)	94.6(2)
C(12)−N(5)−Al(1)	129.9(8)	C(32)−N(10)−Al(2)	132.4(8)	C(15)−N(5)−Al(2)	130.0(3)	N(5)−C(12)−O(1)	127.1(5)
C(13)−N(5)−Al(1)	113.0(8)	C(33)−N(10)−Al(2)	111.1(7)	C(16)−N(5)−Al(2)	112.1(3)	N(5)−C(12)−C(11)	115.2(5)
N(5)−C(12)−C(11)	118(1)	N(10)−C(32)−C(31)	116.6(9)	N(5)−C(15)−C(14)	117.1(4)	O(1)−C(12)−C(11)	117.4(5)
						C(12)−O(1)−Al(1)	131.4(3)

of 2,6-dimethylphenol afforded the corresponding bis-aryloxide aluminum derivatives (Scheme 4). The reactions were carried out at room temperature in toluene solution for 16 h to give very good yields of $[Al(OR)_2\{\kappa^2\text{-sbpam}\}]$ (**11**) and $[Al(OR)_2\{\kappa^2\text{-}(S)\text{-mbpam}\}]$ (**12**) (R = 2,6-$Me_2C_6H_3O$) (>90%). Complex **12** was obtained as an enantiopure compound.

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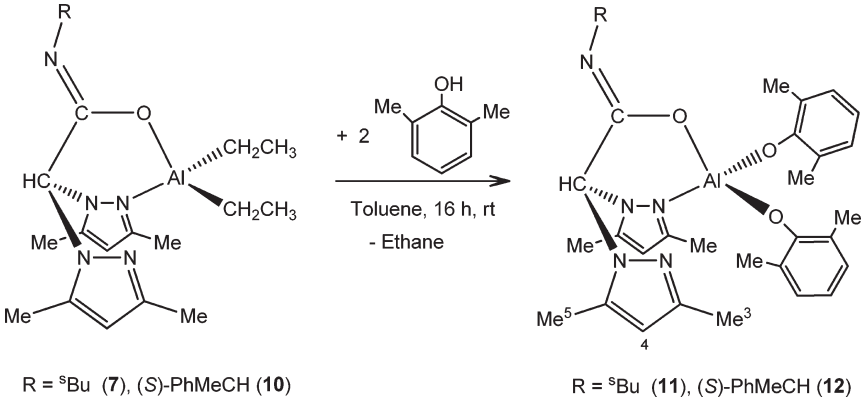
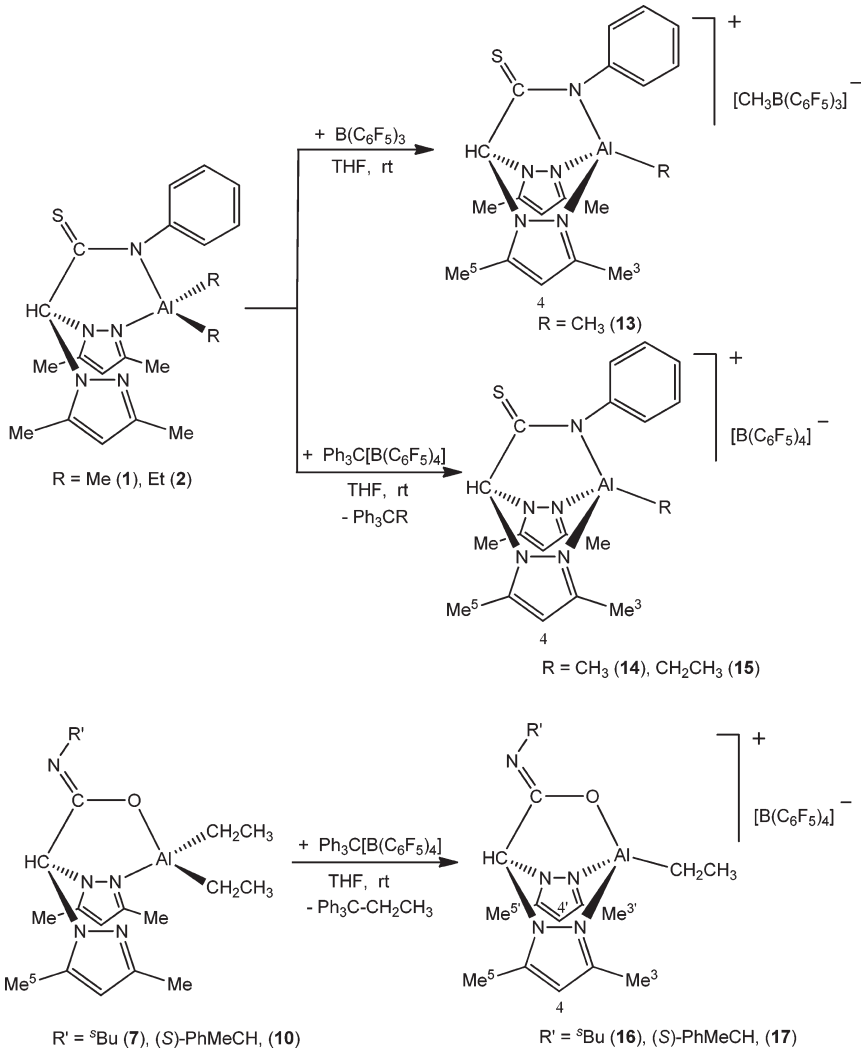
Scheme 4. Summary of the Reaction Leading to Complexes 11 and 12



Scheme 5. Summary of Reactions Leading to Cationic Complexes 13−17



The room-temperature ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **11** and **12**, both of which have a stereogenic carbon, show two singlets for some of the H^4, Me^3, and Me^5 pyrazole protons and carbons, some of which appear broad. Moreover, resonances for the *o*-methyl groups of the aryloxide substituents appear as broad singlets. The broadness of some ^{1}H NMR signals of the heteroscorpionate ligand and aryloxide groups in compounds **11** and **12** suggest that dynamic behavior must exist between pyrazole rings,

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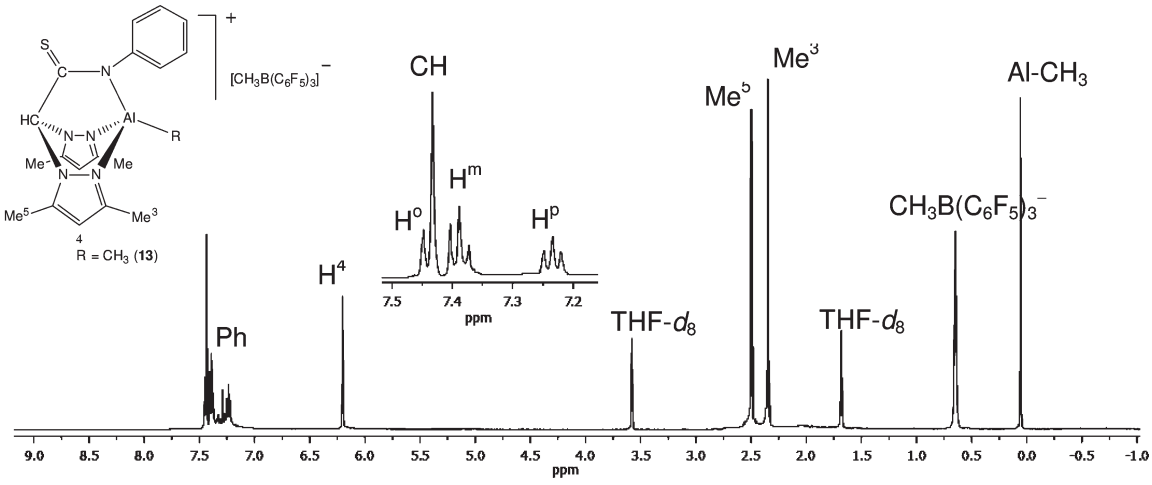

Figure 5. Room-temperature ^{1}H NMR spectrum of the complex [AlMe{κ^3-pbptam}][MeB(C_6F_5)$_3$] (**13**).

and different isomers might be present in slow exchange as with the bis(alkyl) precursors. The variable-temperature (VT) NMR analysis shows that at subambient temperature the resonances of the methyl group on the aryloxide ligands, along with those of the pyrazole rings and the resonance of H^4 of the same rings, broaden and resolve into two separate peaks. At −100 °C, the resonances become well-resolved and the NMR spectra become consistent with a tetrahedral structural disposition with a κ^2NO coordination mode of the acetamidate heteroscorpionate ligand, with two aryloxide ligands occupying the other two coordination positions (see Scheme 4).

Cationic aluminum complexes are of particular interest, due to the enhancement of the Lewis acidity of the aluminum center, a characteristic that can be associated with higher ROP activity. In this context, cationic complexes have already found application in lactide and lactone polymerization.[17g,22] Tetracoordinate cationic heteroscorpionate complexes can be particularly attractive, due to the combination of cationic charge and low coordination number producing increased electrophilic character at the metal. The ionization of dialkyl aluminum complexes **1**, **2**, **7**, and **9** were studied with the alkyl abstracting reagents B(C_6F_5)$_3$ and [Ph_3C][B(C_6F_5)$_4$]. Addition of 1 equiv of the borane B(C_6F_5)$_3$ to the methyl derivative **1** in THF-d_8 gave the cationic species [AlMe{κ^3-pbptam}][MeB(C_6F_5)$_3$] (**13**) (Scheme 5). The salt, which was stable for days in THF-d_8, could not be isolated in a pure form due to its oily nature. The solution structure of aluminum cation **13** was deduced from ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data (THF-d_8 at room temperature). The ^{1}H NMR spectrum of **13** (Figure 5) at room temperature shows a singlet for each of the H^4, Me^3, and Me^5 pyrazole protons, indicating that the pyrazoles are equivalent, and a sharp singlet for the methyl ligand. It is worth noting that the pyrazole proton signals are sharp and well-resolved even at low temperatures (ca. −90 °C), indicating the elevated coordination energy of the ligand with the aluminum center and the absence of any fluxional equilibrium involving the neutral moiety of the ligand. The signal for the methyl group of the [MeB(C_6F_5)$_3$]$^-$ anion appeared at 0.70 ppm, indicating that the anion was substantially not coordinated to the aluminum cation.[17g] The noncoordinating nature of the [MeB(C_6F_5)$_3$]$^-$ anion is further confirmed by the small chemical shift difference ($\Delta\delta$ = 3.7 ppm) between the *m*- and *p*-fluorine ^{19}F NMR resonances.[23] These data are consistent with both pyrazole rings being coordinated to the cationic center, forming a tetracoordinate alkyl aluminum cation with a C_s-symmetric structure, which is consistent with a κ^3NNN coordination of the heteroscorpionate ligand (Scheme 5). Additionally, responses in the ^{1}H NOESY-1D experiments from protons in the R−N moiety and Me^3 of the pyrazole rings on irradiating the Al−CH_3 protons support the κ^3NNN coordination mode and the lack of response in the ^{1}H NOESY-1D experiment from the methyl group of the anion on irradiating the Al−CH_3 protons or on irradiating the Me^3 protons of the pyrazole rings supports the noncoordinating nature of the [MeB(C_6F_5)$_3$]$^-$ anion.

The use of the trityl salt [Ph_3C][B(C_6F_5)$_4$] allowed access to well-defined aluminum cation moieties derived from **1**, **2**, **7**, and **10**. The reaction of Al−methyl **1** and the diethyl aluminum complexes **2**, **7**, and **10** with [Ph_3C][B(C_6F_5)$_4$] led to the quantitative formation of the aluminum cations [AlMe{κ^3-pbptam}]$^+$ (**14**), [AlEt{κ^3-pbptam}]$^+$ (**15**), [AlEt{κ^3-sbpam}]$^+$ (**16**), and [AlEt{κ^3-(*S*)-mbpam}]$^+$ (**17**), respectively (Scheme 5). These compounds were fully dissociated [B(C_6F_5)$_4$]$^-$ salts, as evidenced by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy (see the Experimental Section). The salt species **14**−**17** are stable for days in THF-d_8 at room temperature. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **14** and **15** (nonchiral compounds) exhibit a sharp singlet for each of the H^4, Me^3, and Me^5 pyrazole protons, indicating that the pyrazole rings are equivalent. However, the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra of complexes **16** and **17** (chiral compounds) show two sharp singlets for each of the H^4, Me^3, and Me^5 pyrazole protons. The spectroscopic data obtained under the conditions investigated are consistent with an overall C_1-symmetric structure with an effective κ^3 coordination of the corresponding heteroscorpionate ligand to the cationic aluminum center (Scheme 5). In addition, the AlMe or AlEt resonances are shifted upfield relative to the corresponding resonances in dialkyl complexes (see the Experimental Section), and this is the result of the cationic charge on the aluminum center. In a way similar to that for complex **13**, resonances for cationic derivatives **14**−**17** are sharp and well-resolved even at low temperature, indicating the elevated coordination energy of the ligand to the metal center and the absence of any fluxional equilibrium involving the neutral moiety of the ligand.

Polymerization Studies. A good initiator for the ROP of cyclic esters requires a redox-inactive metal, an inorganic

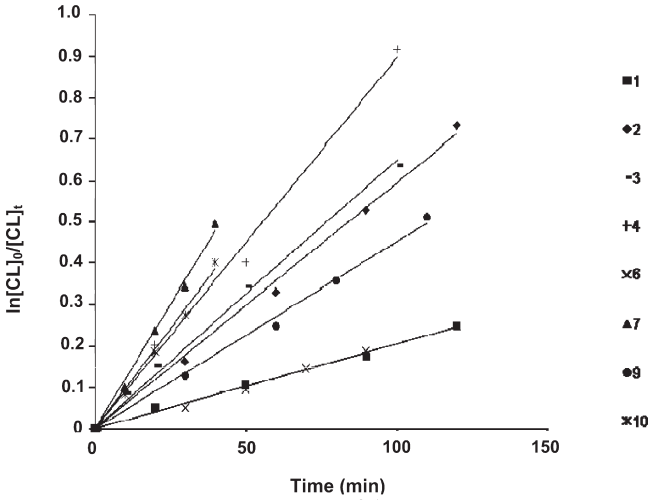

Figure 6. First-order kinetic plots for CL polymerizations in toluene at 70 °C with [CL]/[Al] = 500 and [Al] = 4.5×10^{-3} mol L^{-1}: **1**, k_{app} = 2.0×10^{-3} s^{-1} (linear fit, R = 0.997); **2**, k_{app} = 5.9×10^{-3} s^{-1} (linear fit, R = 0.998); **3**, k_{app} = 6.5×10^{-3} s^{-1} (linear fit, R = 0.997); **4**, k_{app} = 9.0×10^{-3} s^{-1} (linear fit, R = 0.997); **6**, k_{app} = 2.0×10^{-3} s^{-1} (linear fit, R = 0.997); **7**, k_{app} = 11.9×10^{-3} s^{-1} (linear fit, R = 0.997); **9**, k_{app} = 4.5×10^{-3} s^{-1} (linear fit, R = 0.997); **10**, k_{app} = 9.6×10^{-3} s^{-1} (linear fit, R = 0.997).

template L_nM that is inert with respect to undesirable reactions, and a labile ligand able to undergo an insertion reaction with C−X multiple bonds. In this context, β-diketiminate and Schiff base aluminum complexes have displayed good catalytic activity in the ROP of cyclic esters, and most of these examples are aluminum alkoxide or alkyl complexes plus a cocatalyst such as BnOH or ^{i}PrOH. To the best of our knowledge, very few alkyl complexes without a cocatalyst have been used as successful initiators for the ROP of cyclic esters.[4a,11l,17h,18g,24]

Given that the alkyl compounds **1**−**10** are thermally robust and resistant toward hydrolysis, properties which suggest that these compounds might be useful in catalytic processes that require relatively high temperatures, we investigated them as initiators for the ROP of lactide and lactones. We first studied the catalytic performance—namely activity and degree of control—in the assessment of the ring-opening polymerization of ε-CL. The activities of these compounds were evaluated by comparison of the kinetics parameters. For this purpose, the polymerization of ε-CL was monitored in time by manual sampling followed by ^{1}H NMR analysis to determine the degree of monomer conversion. The polymerization kinetics were studied for complexes **1**−**10** with $[\varepsilon\text{-CL}]_0/[\text{Al}]$ = 500 and [Al] = 4.5×10^{-3} M at 70 °C using toluene as solvent and without cocatalyst or activator. A semilogarithmic plot of $\ln([\varepsilon\text{-CL}]_0/[\varepsilon\text{-CL}]_t)$ versus reaction time is shown in Figure 6, where $[\varepsilon\text{-CL}]_0$ is the initial lactone monomer concentration and $[\varepsilon\text{-CL}]_t$ the lactone concentration at a given reaction time t. In all cases, the linearity of the plot shows that the propagation was first order with respect to lactone monomer when polymerized at 70 °C in toluene and an induction period was not observed. The absence of an induction period indicates that the initiators were reactive from the beginning; i.e., rearrangement of initiator aggregates was not necessary to form active species. The linearity of the plot also illustrates that termination reactions did not occur during the polymerization. The fastest polymerization for ε-CL was observed for the ethyl derivatives. The k_{app} values for the monomeric ethyl acetamidate derivatives **4**, **7**, and **10** were of the same order of magnitude and roughly 1 order higher than the k_{app} value found for the ethyl thioacetamidate complex **2**. The methyl derivatives **1** and **6** presented the lowest k_{app} values under the same conditions. In the case of the isobutyl derivatives **5** and **8**, the initiation rate must be very slow and only traces of polymer were formed, probably due to the steric hindrance of the isobutyl groups on aluminum retarding the interaction between the Al center and lactones.

Ethyl initiators **2**, **4**, **7**, and **10** acted as efficient single-component catalysts for the polymerization of ε-CL to give medium-high molecular weight polymers; the results of these experiments are collected in Table 3. A variety of polymerization conditions were explored for compound **7**. Complex **7** initiated very rapid polymerization of ε-CL at 70 °C (entry 7) and gave 40% conversion of 500 equiv of ε-CL in 0.66 h (see M_n vs conversion in Figure S11 in the Supporting Information). The polymerization provided a medium-high molecular weight polymer with a medium broad polydispersity (M_n = 29 460, M_w/M_n = 1.17). When the reaction time was extended to 2 h (entry 11), almost complete conversion was observed (85%) with an increase in the molecular weight distribution (M_w/M_n = 1.38, entry 11). Not unexpectedly, an increase in the temperature up to 130 °C led to complete conversion of the monomer in 0.033 h with a higher polydispersity index (M_w/M_n = 2.01, entry 12). As expected, when the reaction solvent was changed to THF, only 35% of the monomer was converted in 4 h and a decrease in molecular weight was observed (M_n = 24 900, entry 13). These changes are due to coordination of the THF molecule, a process that competes with monomer molecules in the polymerization process. In these tests polymer molecular weights were obtained by using a monomer to initiator ratio of 500:1. An increase in this ratio by a factor of 2 gave polymer with a significantly higher molecular weight, while the molecular weight distribution was more or less maintained (entry 14). Two possibilities can account for the relatively moderate to broad polydispersities observed with the ethyl derivatives at 70 °C. First, in principle the use of an Al−alkyl group as an initiator, which is known to be less nucleophilic than alkoxide, leads to a delay in comparison to propagation.[25] Second, back-biting reactions or transesterifications can take place as side reactions and these result in the formation of macrocycles with a wide range of molecular weight distributions. The M_n values measured by gel permeation chromatography (GPC) were substantially higher than those predicted on the basis of conversion and on the assumption that each aluminum center is catalytically active. This deviation could be consistent with poor rates of initiation (ε-CL initiation in the Al−Et bond) compared to propagation, which is a well-established feature of metal alkyl initiators.[9b,26]

The most active organoaluminum initiators in the ROP of ε-CL (ethyl derivatives **2**, **4**, **7**, and **10**) were tested in lactide polymerization (Table 4). Derivatives **2**, **4**, **7**, and **10** were examined for polymerization of L-LA at 110 °C in toluene without cocatalyst or activator. The resulting PLA had a molecular weight in close agreement with the calculated value for one polymer chain per metal center (entries 1−4), and the GPC data of the polyesters obtained exhibit a monomodal weight distribution. Although the values of M_w/M_n are somewhat higher than those expected for a purely living polymerization (M_w/M_n < 1.1), the overall results are consistent with a controlled polymerization model (see M_n vs conversion in Figure S12 in the Supporting Information). The polymerization occurred without observable

Table 3. Polymerization of ε-Caprolactone Catalyzed by Alkyl Complexes 1−10 and Cationic Complexes 13 and 14[a]

entry	initiator	time (h)	conversn (%)[e]	M_n(theor) (Da)[f]	M_n(exptl) (Da)[g]	M_w/M_n
1	**1**	14	95	54 150	74 780	1.45
2	**2**	8	70	39 900	45 320	1.36
3	**3**	4	72	41 040	43 940	1.32
4	**4**	3	84	47 880	65 736	1.47
5	**5**	16	traces	n.d.[h]	n.d.	n.d.
6	**6**	1.5	47	26 790	44 170	1.42
7	**7**	0.66	40	22 800	29 460	1.17
8	**8**	16	traces	n.d.	n.d.	n.d.
9	**9**	5	56	31 920	36 072	1.28
10	**10**	3.5	87	49 590	74 970	1.49
11	**7**	2	85	48 450	53 887	1.38
12	**7**[b]	0.033	98	55 860	82 030	2.01
13	**7**[c]	4	35	19 950	24 900	1.26
14	**7**[d]	1.5	97	110 580	127 734	1.41
15	**13**	0.66	40	22 800	57 130	1.63
16	**14**	0.66	50	28 500	61 790	1.65

[a] Polymerization conditions: 90 μmol of initiator, 20 mL of toluene as solvent, $[\varepsilon\text{-CL}]_0/[\text{initiator}]_0 = 500$, 70 °C. [b] 130 °C. [c] THF as solvent. [d] $[\varepsilon\text{-CL}]_0/[\text{initiator}]_0 = 1000$. [e] Percentage conversion of the monomer: (weight of polymer recovered)/(weight of monomer) × 100. [f] Theoretical M_n = (monomer/initiator) × (% conversion) × (M_w of ε-CL). [g] Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental M_n was calculated considering Mark−Houwink's corrections for M_n (M_n(exptl) = 0.56[M_n(GPC)]). [h] n.d. = not determined.

Table 4. Polymerization of Lactide Catalyzed by Complexes 2, 4, 7, and 10[a]

entry	initiator	monomer	time (h)	conversn (%)[d]	M_n(theor) (Da)[e]	M_n(exptl) (Da)[f]	M_w/M_n
1	**2**	L-LA	3	60	17 280	20 520	1.21
2	**4**	L-LA	3	80	23 040	30 100	1.26
3	**7**	L-LA	2	82	23 616	21 950	1.16
4	**10**	L-LA	3	72	20 736	22 300	1.15
5	**7**[b]	L-LA	2	90	25 920	34 410	1.32
6	**2**	*rac*-LA	15	98	28 224	32 880	1.26
7	**4**	*rac*-LA	6.5	64	18 432	28 740	1.23
8	**7**	*rac*-LA	6	83	23 904	26 090	1.17
9	**7**[b]	*rac*-LA	2	90	25 920	51 010	1.53
10	**7**[c]	*rac*-LA	0.15	85	24 480	21 980	2.47
11	**10**	*rac*-LA	16	30	8 640	12 580	1.11

[a] Polymerization conditions: 90 μmol of initiator, 20 mL of toluene as solvent, $[\text{LA}]_0/[\text{initiator}]_0 = 200$, 110 °C. [b] 130 °C. [c] Solvent free. [d] Percentage conversion of the monomer: (weight of polymer recovered)/(weight of monomer) × 100. [e] Theoretical M_n = (monomer/initiator) × (% conversion) × (M_w of LA). [f] Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental M_n was calculated considering Mark−Houwink's corrections for M_n (M_n(exptl) = 0.56[M_n(GPC)]).

epimerization reactions at the chiral centers, as evidenced by the single resonance at δ 5.2 ppm in the methine region (P_m[27] > 0.90) in the homonuclear decoupled ^{1}H NMR spectrum (Figure S13 in the Supporting Information), and afforded highly crystalline, isotactic polymers with T_m values in the range 168−172 °C. The low level of stereochemical imperfections was also revealed in the poly(L-lactide) with M_n > 15 000, where the optical activity remained almost constant: $[\alpha]_D^{22}$ = 145−148°. It is important to note that the PLAs obtained had the same tacticities regardless of the heteroscorpionate ligand used as a scaffold. An increase in the temperature up to 130 °C for compound **7** led to higher productivity without any observable change in tacticity. Once again, acetamidate derivatives gave higher conversions than the thioacetamidate counterparts (e.g., entry 1 vs 2).

Initiators **2**, **4**, **7**, and **10** were also tested in the polymerization of *rac*-lactide in toluene at 110 °C without cocatalyst or activator (entries 6−11). Derivative **7** gave 83% conversion of 200 equiv after 6 h (entry 8) and produced medium molecular weight material with a very narrow polydispersity (M_n = 26 090, M_w/M_n = 1.17), while 90% of the polymer was recovered after 2 h at 130 °C with a broader polydispersity (M_w/M_n = 1.53, entry 9). We can attribute this broad molecular weight distribution to a small degree of transesterification and/or slow and incomplete initiation relative to propagation. In all cases (entries 6−11), low-melting materials were obtained with the T_m ranging from 127 to 140 °C. As far as we are aware, very few examples of aluminum alkyl initiators without cocatalyst have been reported to act as active single-site catalysts for the ROP of *rac*-lactide.[11l,18g] Microstructural analysis of the poly(*rac*-lactide) by ^{1}H NMR spectroscopy revealed that these initiators exert a low degree of stereoselectivity (P_m values of around 0.50).[28] This behavior during the propagation is most probably the result of the low steric demand of the methyl substituents in the two pyrazole rings. This leads to sterically less congested, more flexible, and

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therefore less selective active centers to the incoming lactide. These results parallel those reported by Sadow et al.,[18g] who described systems that polymerized *rac*-lactide to atactic poly(lactide) by means of alkyl aluminum initiators without the addition of cocatalysts.

PLAs can be synthesized by both solution polymerization and bulk polymerization. However, the solution polymerization suffers from certain disadvantages such as being susceptible to the impurity level. The bulk polymerization is thus often preferred for the large-scale production of PLAs.[29] With regard to the design of new initiators for our ROP studies, we became interested in exploring the organoaluminum derivate **7** as an initiator for the bulk polymerization of *rac*-lactide. In the polymerization procedure the monomer *rac*-lactide and the initiator (*rac*-LA to Al ratio of 200) were heated to 130 °C. Complex **7** initiated very rapid polymerization of *rac*-LA under bulk conditions (entry 10) and gave 85% conversion of 200 equiv of *rac*-LA in 0.15 h. Under bulk conditions complex **7** afforded lower molecular weight and higher molecular weight distributions than in solution. This change may be caused by a high level of side reactions such as interchain and intrachain transesterification , which result in a chain-transfer reaction. The P_m value of 0.5 implies that the use of this complex under bulk conditions does not affect the tacticity of the resulting polymer. Unfortunately, the aryloxide derivatives $[Al(OR)_2\{\kappa^2\text{-sbpam}\}]$ (**11**) and $[Al(OR)_2\{\kappa^2\text{-}(S)\text{-mbpam}\}]$ (**12**) (R = 2,6-$Me_2C_6H_4O$) did not initiate the ROP of lactones and lactides under the same conditions.

The structure and chemical composition of PLA polymers obtained by **7** were also studied by matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF MS), using dithranol as matrix. In order to avoid multiple species formation, pure methanol was used to quench the polymerization after reaction on polymers for MALDI-TOF analysis. Spectra were recorded in reflection mode using a positive ion extraction. As this is a soft technique, polymers can be detected as intact molecular adducts; MALDI-TOF MS spectra can be used to determine the size of repeat units as well as initiator-group and end-group masses, M_n and M_w, and thus M_w/M_n, as long as the polymer molecular weight distribution is not too high. However, detectors usually induce mass discrimination effects at high masses and the ionization of species is not independent of their size. As a result, accurate estimates of average molecular weights by MALDI-TOF are limited to nearly monodisperse polymer samples. In our case, PLA polymers prepared are out of the determination range of M_w/M_n by MALDI-TOF; however, the structural composition of the polymer can be characterized by this technique. Typical MALDI-TOF MS spectra of PLA polymer prepared with this catalyst show a monotonic decrease distribution of peaks because of the already mentioned high molecular weight distribution (Figure S14 in the Supporting Information). The mass spectrum shows a cluster of homologous peaks separated by a molecular mass corresponding to the repeating unit of the analyzed polymer. This peak separation was found to be 72.0 Da and corresponds to just one lactate unit ($C_3H_4O_2$). The *rac*-lactide molecule contains two lactate units, and in principle, it would be expected that peak separation in the mass spectrum would be 144.0 Da instead of 72.0 Da. Nevertheless, as previously mentioned, an intermolecular transesterification reaction will result in a fast interchange of the chain length and consequently the formation of not only the even numbers of lactate repeating units but also all possible combinations. This high degree of intermolecular transesterification could justify the high molecular weight distribution as well as the fact that no peaks associated to internal transesterification reaction (back-biting) are found in the mass spectra of these polymers. The mass spectrum also reveals that the chemical composition of the polymer is in agreement with an ethyl initiator group and a methoxy end group, as $[M]^+$ and $[M + Na]^+$ ions are detected in the measurements. As an example, Figure S14 in the Supporting Information shows peaks at 1844.59 Da ($[M]^+$) and 1867.58 Da ($[M + Na]^+$) that correspond to a polymer containing 24 lactate repeating units, an ethyl initiator group, and a methoxy end group.

The cationic complexes $[AlMe\{\kappa^3\text{-pbptam}\}][MeB(C_6F_5)_3]$ (**13**) and $[AlEt\{\kappa^3\text{-pbptam}\}][B(C_6F_5)_4]$ (**14**), generated in situ by addition of the abstracting reagents $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$ to $[AlMe_2\{\kappa^2\text{-pbptam}\}]$ (**1**), were tested as initiators for the ROP of of ε-CL. These compounds initiated very rapid polymerization at 70 °C and gave almost 50% conversions of 500 equiv of ε-CL in 45 min (entries 15 and 16 in Table 3). Compounds **13** and **14** were significantly more active initiators in the ROP of ε-CL than the dialkyl aluminum precursor **1**. This marked difference in reactivity between the types of species is presumably a consequence of the fundamental mechanistic differences in their polymerization performances.[30] It has been established that polymerization can be envisaged to occur by either transfer of the nucleophilic alkyl ligand to the monomer, with formation of a metal alkoxide propagating species, or ring opening and propagation through a cationic mechanism.[31] The higher polydispersities obtained with complexes **13** and **14** point to a cationic mechanism, where the initial formation of a carbocationic species is followed by a propagation step. Finally, the cationic species **13** and **14** did not show activity in the ROP of lactides.

CONCLUSIONS

In conclusion, we report here the facile synthesis of a new family of dialkyl heteroscorpionate aluminum compounds bearing an acetamidate or thioacetamidate as pendant donor arms. NMR, VT NMR, and X-ray single-crystal studies allowed κ^2NO and κ^2NN coordination modes to be established for the acetamidate- and thioacetamidate-containing complexes, respectively. The solid-state structure is not retained in solution, and fluxional exchange between coordinated and noncoordinated pyrazole rings of the heteroscorpionate ligands is observed. Subsequent reaction of some of the dialkyl compounds with a phenol or alkyl abstracting reagents gave rise to the corresponding aryloxide and cationic derivatives. A series of detailed studies of ROP processes involving the different types of isolated complexes were undertaken. ε-Caprolactone was polymerized to give medium molecular weight polymers with moderate to broad polydispersities. The broader polydisperities are due to the poor rates of initiation compared to propagation, which is a well-established feature of metal alkyl initiators. Not surprisingly, the polymerization of LA occurred more slowly than that of ε-CL but offered better control. L-Lactide afforded highly crystalline, isotactic PLA materials with medium molecular weights, narrow polydispersities, and very high melting temperatures. Propagation occurred without observable epimerization with all families of initiators. Polymerization of *rac*-lactide did not result in appreciable levels of selectivity and produced atactic PLAs. Further iterations of ligand design will be required to find catalysts capable of achieving stereochemical control under solution ROP conditions.

EXPERIMENTAL SECTION

All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, *n*-hexane) and distilled under nitrogen from sodium (toluene) or sodium−potassium alloy (*n*-hexane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova FT-500 spectrometer and referenced to the residual deuterated solvent. The NOESY-1D spectra were recorded with the following acquisition parameters: irradiation time 2 s and number of scans 256, using standard VARIANT-FT software. Two-dimensional NMR spectra were acquired using standard VARIANT-FT software and processed using an IPC-Sun computer. $AlMe_3$, $AlEt_3$, Al^iBu_3, *rac*-lactide, L-lactide, $B(C_6F_5)_3$, and 2,4,6-trimethylphenol were purchased from Aldrich. ε-Caprolactone was purchased from Alfa-Aesar and $[Ph_3C][B(C_6F_5)_4]$ from STREM. The ligands pbpamH, sbpamH, (*S*)-mbpamH, and pbptamH were prepared according to literature procedures.[20] ε-Caprolactone was dried by stirring over fresh CaH_2 for 48 h and then distilled under reduced pressure and stored over activated 4 Å molecular sieves. L-Lactide and *rac*-lactide were sublimed three times, recrystallized from THF, and finally sublimed again prior to use. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a TSK-GEL G3000H column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 50 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580−483 000 Da. PLA melting temperatures were measured using a SMP10 melting point apparatus. The sample was heated to 100 °C and then heated at a rate of 1 °C/min to 185 °C. The specific rotation $[\alpha]_D^{22}$ was measured at 22 °C on a Perkin-Elmer 241 polarimeter equipped with a Na lamp operating at 589 nm with a light path length of 10 cm. The MALDI-TOF spectra were acquired using a Bruker Autoflex II TOF/TOF spectrometer using dithranol (1,8,9-trihydroxyanthracene) as matrix material. Samples cocrystallized with matrix in a 100:1 ratio on the probe were ionized in positive reflector mode. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700−3200 Da) and Protein Calibration Standard I (covered mass range: 5000−17 500 Da).

Synthesis of 1. In a 250 cm^3 Schlenk tube, pbptamH (pbptam = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide; 0.85 g, 2.50 mmol) was dissolved in dry toluene (70 mL) and cooled to 0 °C. A solution of $AlMe_3$ (2 M in toluene; 1.25 mL, 2.50 mmol) was added, and the mixture was warmed to room temperature and stirred for 1 h. The solution was concentrated and recrystallized at −26 °C to give compound **1** as yellow crystals. Yield: 0.89 g, 90%. Anal. Calcd for $C_{20}H_{26}AlN_5S$: C, 60.74; H, 6.63; N, 17.71. Found: C, 60.95; H, 6.84; N, 17.58. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 7.44 (s, 1H, CH), 7.38 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o NPh), 7.20 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.03 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, H^p NPh), 5.34 (s, 2H, H^4), 2.05 (s, 6H, Me^3), 1.94 (s, 6H, Me^5), −0.18 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K; δ (ppm)): 194.9 (NC═S), 146.5, 150.4, 142.3 (C$^{3\text{ or }5}$, C^{ipso} NPh), 129.2 (C^o NPh), 127.3 (C^m NPh), 126.3 (C^p NPh), 107.5 (C^4), 75.8 (CH), 13.1 (Me^3), 11.2 (Me^5), −8.1 (Al CH_3).

Synthesis of 2. The synthesis of **2** was carried out in a manner identical with that for **1**, using pbptamH (pbptam = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)thioacetamide; 0.85 g, 2.50 mmol) and $AlEt_3$ (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 0.95 g, 90%. Anal. Calcd for $C_{22}H_{30}AlN_5S$: C, 62.39; H, 7.14; N, 16.53. Found: C, 61.98; H, 7.34; N, 16.31. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 7.44 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, H^o NPh), 7.43 (s, 1H, CH), 7.22 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.04 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, H^p NPh), 5.34 (s, 2 H, H^4), 2.09 (s, 6H, Me^5), 1.91 (s, 6H, Me^3), 1.23 (t, $^3J_{H-H}$ = 8.0 Hz, 6H, $AlCH_2CH_3$), 0.50 (m, 4 H, $AlCH_2CH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K; δ (ppm)): 195.1 (NC═S), 150.5, 149.4, 142.5 (C$^{3\text{ or }5}$, C^{ipso} NPh), 129.2 (C^o NPh), 126.9 (C^m NPh), 126.4 (C^p NPh), 107.5 (C^4), 75.8 (CH), 13.0 (Me^5), 11.0 (Me^3), 9.5 ($AlCH_2CH_3$), 0.9 ($AlCH_2CH_3$).

Synthesis of 3. The synthesis of **3** was carried out in a manner identical with that for **1**, using pbpamH (pbpamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.79 g, 2.50 mmol) and $AlMe_3$ (2 M in toluene; 1.25 mL, 2.50 mmol). Yield: 0.82 g, 86%. Anal. Calcd for $C_{20}H_{26}AlN_5O$: C, 63.31; H, 6.91; N, 18.46. Found: C, 63.11; H, 6.69; N, 18.13. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 7.64 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o NPh), 7.28 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.02 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p NPh), 6.63 (s, 1H, CH), 5.37 (s, 2H, H^4), 1.96 (s, 6H, Me^3), 1.90 (s, 6H, Me^5), −0.25 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K), δ (ppm): 155.3 (NC═O), 149.4, 147.8, 140.4 (C$^{3\text{ or }5}$, C^{ipso} NPh), 128.8 (C^m NPh), 124.3 (C^o NPh), 124.1 (C^p NPh), 107.6 (C^4), 71.7 (CH), 13.5 (Me^3), 10.7 (Me^5), −8.9 ($AlCH_3$).

Synthesis of 4. The synthesis of **4** was carried out in a manner identical with that for **1**, using pbpamH (pbpamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.79 g, 2.50 mmol) and $AlEt_3$ (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 0.91 g, 89%. Anal. Calcd for $C_{22}H_{30}AlN_5O$: C, 64.84; H, 7.42; N, 17.19. Found: C, 64.98; H, 7.39; N, 17.05. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 7.67 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o NPh), 7.29 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.04 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p NPh), 6.63 (s, 1H, CH), 5.41 (s, 2 H, H^4), 1.99 (s, 6H, Me^3), 1.88 (s, 6H, Me^5), 1.33 (t, $^3J_{H-H}$ = 7.9 Hz, 6H, $AlCH_2CH_3$), 0.40 (m, 4H, $AlCH_2CH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K; δ (ppm)): 154.3 (NC═O), 149.4, 147.9, 140.4 (C$^{3\text{ or }5}$, C^{ipso} NPh), 128.8 (C^m NPh), 124.3 (C^o NPh), 124.1 (C^p NPh), 107.6 (C^4), 71.7 (CH), 13.4 (Me^3), 10.8 (Me^5), 9.2 ($AlCH_2CH_3$), 0.6 ($AlCH_2CH_3$).

Synthesis of 5. The synthesis of **5** was carried out in a manner identical with that for **1**, using pbpamH (pbpamH = *N*-phenyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.79 g, 2.50 mmol) and Al^iBu_3 (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 1.02 g, 88%. Anal. Calcd for $C_{26}H_{38}AlN_5O$: C, 67.36; H, 8.26; N, 15.11. Found: C, 67.11; H, 8.39; N, 15.40. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 7.63 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o NPh), 7.28 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.00 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p NPh), 6.64 (s, 1H, CH), 5.40 (br s, 2H, H^4), 2.12 (br s, 2H, $AlCH_2CH(CH_3)_2$), 2.10 (br s, 6H, Me^3), 1.91 (br s, 6H, Me^5), 1.16 (br s, 12H, $AlCH_2CH(CH_3)_2$), 0.40 (br s, 4H, $AlCH_2CH(CH_3)_2$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K; δ (ppm)): 153.9 (NC═O), 149.4, 147.7, 142.4 (C$^{3\text{ or }5}$, C^{ipso} NPh), 128.6 (C^m NPh), 124.3 (C^o NPh), 124.0 (C^p NPh), 107.6 (C^4), 71.5 (CH), 28.4 ($AlCH_2CH(CH_3)_2$), 26.3 [$AlCH_2CH(CH_3)_2$), 13.6 ($AlCH_2CH(CH_3)_2$), 13.4 (Me^3), 10.8 (Me^5).

Synthesis of 6. The synthesis of **6** was carried out in a manner identical with that for **1**, using sbpamH (sbpamH = *N*-*sec*-butyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.76 g, 2.50 mmol) and $AlMe_3$ (2 M in toluene; 1.25 mL, 2.50 mmol). Yield: 0.76 g, 85%. Anal. Calcd for $C_{18}H_{30}AlN_5O$: C, 60.15; H, 8.41; N, 19.48. Found: C, 60.31; H, 8.19; N, 19.31. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 6.52 (s, 1H, CH), 5.41, 5.35 (s, 2H, H$^{4,4'}$), 4.18 (m, 1H, $NCH(CH_3)(CH_2CH_3)$), 1.99, 1.98 (s, 6H, Me$^{3,3'}$), 1.92, 1.82 (s, 6H, Me$^{5,5'}$), 1.70, 1.60 (m, 4H, $NCH(CH_3)(CH_2CH_3)$), 1.30 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 1.01 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), −0.15 (s, 6H, $AlCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 297 K; δ (ppm)): 153.5 (NC═O), 149.4, 149.3 (C$^{3,3'\text{ or }5,5'}$), 107.4, 107.2 (C$^{4,4'}$), 71.7 (CH), 51.7 ($NCH(CH_3)(CH_2CH_3)$), 31.6 ($NCH(CH_3)(CH_2CH_3)$), 21.4 ($NCH(CH_3)(CH_2CH_3)$), 13.1, 13.0 (Me$^{3,3'}$), 11.3 ($NCH(CH_3)(CH_2CH_3)$), 10.5, 10.6 (Me$^{5,5'}$), −8.8 ($AlCH_3$).

Synthesis of 7. The synthesis of **7** was carried out in a manner identical with that for **1**, using sbpamH (sbpamH = *N*-*sec*-butyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.76 g, 2.50 mmol) and $AlEt_3$ (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 0.89 g, 92%. Anal. Calcd for $C_{20}H_{34}AlN_5O$: C, 61.99; H, 8.84; N, 18.07. Found: C, 61.71; H, 8.59; N, 17.95. ^{1}H NMR (C_6D_6, 297 K; δ (ppm)): 6.51 (s, 1H, CH), 5.42, 5.37 (s, 2H, H$^{4,4'}$), 4.22 (m, 1H, $NCH(CH_3)(CH_2CH_3)$), 2.01 (s, 6H, Me$^{3,3'}$), 1.85 (s, 6H, Me$^{5,5'}$), 1.65 (m, 2H, $NCH(CH_3)(CH_2CH_3)$),

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1.44 (t, $^3J_{H-H}$ = 7.9 Hz, 6H, $AlCH_2CH_3$), 1.31 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 1.00 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 0.47 (m, 4H, $^3J_{H-H}$ = 7.9 Hz, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K; δ (ppm)): 153.6 (NC═O), 149.5, 149.3 ($C^{3,3'\text{ and }5,5'}$), 107.3, 107.2 ($C^{4,4'}$), 71.6 (CH), 51.6 ($NCH(CH_3)(CH_2CH_3)$), 31.5 ($NCH(CH_3)(CH_2CH_3)$), 21.2 ($NCH(CH_3)(CH_2CH_3)$), 13.0 ($Me^{3,3'}$), 11.1 ($NCH(CH_3)(CH_2CH_3)$), 10.6 ($Me^{5,5'}$), 9.3 ($AlCH_2CH_3$), 0.8 ($AlCH_2CH_3$).

Synthesis of 8. The synthesis of **8** was carried out in a manner identical with that for **1**, using sbpamH (sbpamH = *N-sec*-butyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide;0.79 g, 2.50 mmol) and Al^iBu_3 (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 0.95 g, 86%. Anal. Calcd for $C_{24}H_{42}AlN_5O$: C, 64.98; H, 9.54; N, 15.79. Found: C, 65.19; H, 9.22; N, 15.55. ^1H NMR (C_6D_6, 297 K; δ (ppm)): 6.85 (s, 1H, CH), 5.48, 5.19 (s, 2H, $H^{4,4'}$), 4.09 (m, 1H, $NCH(CH_3)(CH_2CH_3)$), 2.22 (br s, 2H, $AlCH_2CH(CH_3)_2$)), 2.01 (s, 6H, $Me^{3,3'}$), 1.85 (s, 6H, $Me^{5,5'}$), 1.75 (m, 2H, $NCH(CH_3)(CH_2CH_3)$), 1.27 (br s, 12H, $AlCH_2CH(CH_3)_2$)), 1.26 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 0.90 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 0.47 (br s, 4H, $AlCH_2CH(CH_3)_2$)). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K; δ (ppm)): 153.4 (NC═O), 149.4, 149.3 ($C^{3,3'\text{ and }5,5'}$), 107.1, 106.9 ($C^{4,4'}$), 71.5 (CH), 51.6 ($NCH(CH_3)(CH_2CH_3)$), 31.7 ($NCH(CH_3)(CH_2CH_3)$), 26.6 ($AlCH_2CH(CH_3)_2$), 26.0 ($AlCH_2CH(CH_3)_2$), 23.4 ($NCH(CH_3)(CH_2CH_3)$), 13.9, 13.8 ($Me^{3,3'}$), 13.7 ($AlCH_2CH(CH_3)_2$), 11.2 ($NCH(CH_3)(CH_2CH_3)$), 11.1, 11.0 ($Me^{5,5'}$).

Synthesis of 9. The synthesis of **9** was carried out in a manner identical with that for **1**, using (*S*)-mbpamH ((*S*)-mbpam*H* = (*S*)-(−)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.79 g, 2.50 mmol) and $AlMe_3$ (2 M in toluene; 1.25 mL, 2.50 mmol). Yield: 0.88 g, 86%. $[\alpha]_D^{25}$ = −21.3° (*c* 0.10, toluene). Anal. Calcd for $C_{22}H_{30}AlN_5O$: C, 64.84; H, 7.42; N, 17.19. Found: C, 64.71; H, 7.39; N, 17.45. ^1H NMR (C_6D_6, 297 K), δ 7.64 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o $NCH(CH_3)Ph$), 7.26 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m $NCH(CH_3)Ph$)), 7.12 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p $NCH(CH_3)Ph$), 6.53 (s, 1H, CH), 5.42 (m, 1H, $NCH(CH_3)Ph$), 5.38, 5.30 (s, 2H, $H^{4,4'}$), 1.99, 1.94 (s, 6H, $Me^{3,3'}$), 1.86, 1.77 (s, 6H, $Me^{5,5'}$), 1.59 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)Ph$), −0.17 (s, 6H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K), δ 153.6 (NC═O), 149.6, 149.3, 147.5 ($C^{3,3'\text{ or }5,5'}$, C^{ipso} $NCH(CH_3)Ph$), 128.3 (C^m $NCH(CH_3)Ph$), 127.3 (C^o $NCH(CH_3)Ph$), 126.4 (C^p $NCH(CH_3)Ph$), 107.4 ($C^{4,4'}$), 71.6 (CH), 54.6 ($NCH(CH_3)Ph$), 24.4 ($NCH(CH_3)Ph$), 13.0 ($Me^{3,3'}$), 10.5 ($Me^{5,5'}$), −8.8 ($AlCH_3$).

Synthesis of 10. The synthesis of **10** was carried out in a manner identical with that for **1**, using (*S*)-mbpamH ((*S*)-mbpamH = (*S*)-(−)-*N*-α-methylbenzyl-2,2-bis(3,5-dimethylpyrazol-1-yl)acetamide; 0.79 g, 2.50 mmol) and $AlEt_3$ (1 M in hexane; 2.50 mL, 2.50 mmol). Yield: 1.01 g, 93%. $[\alpha]_D^{25}$ = −22.4° (*c* 0.10, toluene). Anal. Calcd for $C_{24}H_{34}AlN_5O$: C, 66.18; H, 7.87; N, 16.08. Found: C, 66.23; H, 7.85; N, 15.98. ^1H NMR (C_6D_6, 297 K; δ (ppm)): 7.64 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o $NCH(CH_3)Ph$), 7.26 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m $NCH(CH_3)Ph$), 7.11 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p $NCH(CH_3)Ph$), 6.52 (s, 1H, CH), 5.47 (m, 1H, N $CH(CH_3)Ph$), 5.40, 5.32 (s, 1H, $H^{4,4'}$), 2.01, 1.96 (s, 6H, $Me^{3,3'}$), 1.80 (br s, 6H, $Me^{5,5'}$), 1.61 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)Ph$), 1.39 (br s, 6H, $AlCH_2CH_3$), 0.44 (br s, 4 H, $AlCH_2CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K; δ (ppm)): 153.8 (NC═O), 149.7, 149.4, 147.4 ($C^{3,3'\text{ or }5,5'}$, C^{ipso} $NCH(CH_3)Ph$), 128.3 (C^m $NCH(CH_3)Ph$), 127.3 (C^o $NCH(CH_3)Ph$), 126.4 (C^p $NCH(CH_3)Ph$), 107.4 ($C^{4,4'}$), 71.7(CH), 54.6 ($NCH(CH_3)Ph$), 24.4 ($NCH(CH_3)Ph$), 13.0 ($Me^{3,3'}$), 10.6 ($Me^{5,5'}$), 9.3 ($AlCH_2CH_3$), 0.7 ($AlCH_2CH_3$).

Synthesis of 11. In a 100 cm^3 Schlenk tube, [$AlEt_2\{\kappa^2$-sbpam}] (**7**; 1.00 g, 2.57 mmol) was dissolved in dry toluene (25 mL) at room temperature. A solution of 2,6-dimethylphenol (0.63 g, 5.14 mmol) was added, and the mixture was stirred at room temperature for 16 h. Removal of the volatiles under reduced pressure yielded **11** as a white solid. Yield: 1.32 g, 92%. Anal. Calcd for $C_{32}H_{42}AlN_5O_3$: C, 67.23; H, 7.40; N, 12.25. Found: C, 67.54; H, 7.42; N, 12.09. ^1H NMR (C_6D_6, 297 K; δ (ppm)): 7.56 (s, 1H, CH), 7.01 (d, $^3J_{H-H}$ = 7.0 Hz, 4H, H^m OMe_2Ph), 6.77 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, H^p OMe_2Ph), 5.45 (brs, 2H $H^{4,4'}$), 4.05 (m, 1H, $NCH(CH_3)(CH_2CH_3)$), 2.33 (br s, 12H, OMe_2Ph), 2.01, 2.22 (br s, 12H, $Me^{3,3'\text{ and }}Me^{5,5'}$), 1.30 (m, 2H, $NCH(CH_3)(CH_2CH_3)$), 1.00 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$), 0.79 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)(CH_2CH_3)$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K; δ (ppm)): 155.5 (N *C*═O), 161.9−142.5 ($C^{3,3'\text{ and }5,5'}$, *C* ^{ipso} OMe $_2$Ph), 107.2, 106.9 ($C^{4,4'}$), 76.2 (CH), 51.6 ($NCH(CH_3)(CH_2CH_3)$), 31.5 ($NCH(CH_3)(CH_2CH_3)$), 21.2 ($NCH(CH_3)(CH_2CH_3)$), 11.1 ($NCH(CH_3)(CH_2CH_3)$), 13.0, 12.9 ($Me^{3,3'}$), 10.6, 10.5 ($Me^{5,5'}$), 127.1 (C^m OMe $_2$Ph), 125.6 (C^o OMe $_2$Ph), 114.2 (C^p OMe $_2$Ph), 18.2 (O Me_2Ph).

Synthesis of 12. The synthesis of **12** was carried out in a manner identical with that for **11**, using [$AlEt_2\{\kappa^2$-(*S*)-mbpam}] (**10**; 1.12 g, 2.57 mmol) and 2,6-dimethylphenol (0.63 g, 5.14 mmol). Yield: 1.46 g, 92%. $[\alpha]_D^{25}$ = −35.4° (*c* 0.10, CD_2C_{l2}). Anal. Calcd for $C_{36}H_{42}AlN_5O_3$: C, 69.77; H, 6.83; N, 11.30. Found: C, 69.87; H, 6.94; N, 11.12. ^1H NMR (C_6D_6, 297 K; δ (ppm)): 7.55 (s, 1H, CH), 7.26 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o $NCH(CH_3)Ph$), 7.11 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m $NCH(CH_3)Ph$), 7.07 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, H^p $NCH(CH_3)Ph$), 7.01 (d, $^3J_{H-H}$ = 7.0 Hz, 4H, H^m OMe_2Ph), 6.77 (t, $^3J_{H-H}$ = 7.0 Hz, 2H, H^p OMe_2Ph), 5.46, 5.39 (s, 2H, $H^{4,4'}$), 5.46 (m, 1H, $NCH(CH_3)Ph$), 2.22, 2.10 (br s, 12H, $Me^{3,3'}$ and $Me^{5,5'}$), 1.98 (br s, 12H, OMe_2Ph), 1.39 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, $NCH(CH_3)Ph$). $^{13}C\{^1H\}$ NMR (C_6D_6, 297 K; δ (ppm)): 154.6 (NC═O), 162.8−141.5 ($C^{3,3'\text{ and }5,5'}$, C^{ipso} OMe_2Ph, C^{ipso} $NCH(CH_3)Ph$), 128.3 (C^p $NCH(CH_3)Ph$), 127.9 (C^m $NCH(CH_3)Ph$), 125.4 (C^o $NCH(CH_3)Ph$), 106.3 ($C^{4,4'}$), 75.4 (CH), 55.0 ($NCH(CH_3)Ph$), 20.7 ($NCH(CH_3)Ph$), 16.45, 13.5, 10.4, 10.2 ($Me^{3,3'}$ and $Me^{5,5'}$), 127.6 (C^m OMe_2Ph), 123.3 (C^o OMe_2Ph), 117.9 (C^p OMe_2Ph), 12.5, 12.4 (OMe_2Ph),

Synthesis of 13. In a glovebox, equimolar amounts of [$AlMe_2\{\kappa^2$-pbptam}] (**1**; 0.051 g, 0.13 mmol) and $B(C_6F_5)_3$ (0.067 g, 0.13 mmol) were added to a sample vial and dissolved in 0.6 mL of THF-d_8. The resulting pale yellow solution was transferred to an NMR tube (10 mm o.d.) and analyzed. ^1H NMR (THF-d_8, 297 K; δ (ppm)): 7.45 (d, $^3J_{H-H}$ = 7.0 Hz, 2H, H^o NPh), 7.43 (s, 1H, CH), 7.39 (t, $^3J_{H-H}$ = 6.9 Hz, 2H, H^m NPh), 7.23 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, H^p NPh), 6.20 (s, 2H, H^4), 2.49 (s, 6H, Me^5), 2.35 (s, 6H, Me^3), 0.70 (br s, 3H, $MeB(C_6F_5)_3$), 0.06 (s, 3H, $AlCH_3$). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K; δ (ppm)): 192.8 (NC═S), 154.5, 147,5, 146.5 ($C^{3\text{ or }5}$, C^{ipso} NPh), 129.2 (C^o NPh), 127.3 (C^m NPh), 126.3 (C^p NPh), 111.1 (C^4), 77.7 (CH), 14.6 (Me^3), 11.8 (Me^5), −5.0 ($AlCH_3$), 10.8 ($MeB(C_6F_5)_3$), 140.0−123.4 ($MeB(C_6F_5)_3$). ^{19}F NMR (THF-d_8, 297 K; δ (ppm)): −132.4 (d, $^3J_{F-F}$ = 18.5 Hz, 2F, *o*-C_6F_5), −164.1 (t, $^3J_{F-F}$ = 18.5 Hz, 1F, *p*-C_6F_5), −167.8 (t, $^3J_{F-F}$ = 19.1 Hz, 2F, *m*-C_6F_5).

Synthesis of 14. In a glovebox, equimolar amounts of [$AlMe_2\{\kappa^2$-pbptam}] (**1**; 0.051 g, 0.13 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.12 g, 0.13 mmol) were added to a sample vial and dissolved in 0.6 mL of THF-d_8. The resulting pale yellow solution was transferred to an NMR tube (10 mm o.d.) and analyzed. ^1H NMR (THF-d_8, 297 K; δ (ppm)): 7.60−7.00 (NPh), 7.43 (s, 1H, CH), 6.56 (s, 2H, H^4), 2.53 (s, 6H, Me^3), 2.41 (s, 6H, Me^5), −0.62 (s, 3H, $AlCH_3$), 7.60−7.00 (Ph_3CCH_3), 2.20 (s, 3H, Ph_3CCH_3). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K; δ (ppm)): 191.1 (NC═S), 150.5, 149.3, 147,5 ($C^{3\text{ or }5}$, C^{ipso} NPh) 129.2 (C^o NPh), 126.9 (C^m NPh), 126.4 (C^p NPh), 106.9 (C^4), 75.8 (CH), 12.7 (Me^3), 9.8 (Me^5), −5.5 ($AlCH_3$), 150.5−122.0 (Ph_3CCH_3), 56.5 (Ph_3CCH_3), 12.8 (Ph_3CCH_3), 145.3−122.4 ($B(C_6F_5)_4$). ^{19}F NMR (THF-d_8, 297 K; δ (ppm)): −131.0 (d, $^3J_{F-F}$ = 16.5 Hz, 2F, *o*-C_6F_5), −162.9 (t, $^3J_{F-F}$ = 13.5 Hz, 1F, *p*-C_6F_5), −169.8 (t, $^3J_{F-F}$ = 18.2 Hz, 2F, *m*-C_6F_5).

Synthesis of 15. In a glovebox, equimolar amounts of [$AlEt_2\{\kappa^2$-pbptam}] (**2**; 0.055 g, 0.13 mmol) and $[Ph_3C][B(C_6F_5)_4]$ (0.12 g, 0.13 mmol) were added to a sample vial and dissolved in 0.6 mL of THF-d_8. The resulting pale yellow solution was transferred to an NMR tube

(10 mm o.d.) and analyzed. ^{1}H NMR (THF-d_8, 297 K; δ (ppm)): 7.67 (s, 1H, CH), 7.60−7.00 (NPh), 6.32 (s, 2H, H^4), 2.57, (s, 6H, Me^5), 2.36 (s, 6H, Me^3), 1.09 (t, $^3J_{H-H}$ = 7.9 Hz, 3H,AlCH$_2$C*H*$_3$), 0.05 (m, $^3J_{H-H}$ = 7.9 Hz, 2H, AlC*H*$_2$CH$_3$), 7.40−7.00 (Ph$_3$CCH$_2$CH$_3$), 2.59 (m, 2H, Ph$_3$CC*H*$_2$CH$_3$), 0.87 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, Ph$_3$CCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 297 K; δ (ppm)): 191.9 (N*C*═S), 157.8, 150.2, 147,8 (C$^{3\text{ or }5}$, C^{ipso} NPh), 124.3 (C^o NPh), 128.8 (C^m NPh), 124.1 (C^p NPh), 110.4 (C^4), 76.3 (CH), 13.1 (Me^3), 10.2 (Me^5), 9.2 (AlCH$_2$CH$_3$), 0.6 (AlCH$_2$CH$_3$), 150.5−128.0 (*Ph*$_3$CCH$_2$CH$_3$), 54.1 (Ph$_3$CCH$_2$CH$_3$), 26.9 (Ph$_3$CCH$_2$CH$_3$), 8.1 (Ph$_3$CCH$_2$CH$_3$). 144.8−122.0 (B(*C*$_6$F$_5$)$_4$). ^{19}F NMR (THF-d_8, 297 K; δ (ppm)): −132.5 (d, $^3J_{F-F}$ = 17.1 Hz, 2F, *o*-C$_6$F$_5$), −164.2 (t, $^3J_{F-F}$ = 15.3 Hz, 1F, *p*-C $_6$F$_5$), −167.7 (t, $^3J_{F-F}$ = 16.2 Hz, 2F, *m*-C $_6$F$_5$).

Synthesis of 16. In a glovebox, equimolar amounts of [AlEt$_2${κ^2-sbpam}] (**7**; 0.050 g, 0.13 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.12 g, 0.13 mmol) were added to a sample vial and dissolved in 0.6 mL of THF-d_8. The resulting pale yellow solution was transferred to an NMR tube (10 mm o.d.) and analyzed. ^{1}H NMR (THF-d_8, 297 K; δ (ppm)): 7.02 (s, 1H, CH), 6.25, 6.16 (s, 2H, H$^{4,4'}$), 4.13 (m, 1H, NC*H*(CH$_3$)(CH$_2$CH$_3$)), 2.37, 2.28 (s, 6H, Me$^{5,5'}$), 2.32, 2.25 (s, 6H, Me$^{3,3'}$), 1.60 (m, 2H, NCH(CH$_3$)(C*H*$_2$CH$_3$)), 1.27 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, NCH(C*H*$_3$)(CH$_2$CH$_3$)), 0.94 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, NCH(CH$_3$)(CH$_2$C*H*$_3$)), 0.92 (t, $^3J_{H-H}$ = 9.0 Hz, 3H, AlCH$_2$C*H*$_3$), 0.02 (m, $^3J_{H-H}$ = 7.9 Hz, 2H, AlC*H*$_2$CH$_3$), 7.40−7.00 (Ph$_3$CCH$_2$CH$_3$), 2.48 (m, 2H, Ph$_3$CC*H*$_2$CH$_3$), 0.90 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, Ph$_3$CCH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 297 K; δ (ppm)): 166.6 (N*C*═O), 154.3, 153.2, 145.6, 144.3 (C$^{3,3'\text{ and }5,5'}$), 110.2, 110.0 (C$^{4,4'}$), 67.9 (CH), 51.6 (NCH(CH$_3$)(CH$_2$CH$_3$)), 29.3 (NCH(CH$_3$)(CH$_2$CH$_3$)), 19.1 (NCH(*C*H$_3$)(CH$_2$CH$_3$)), 11.0 (NCH(CH$_3$)(CH$_2$CH$_3$)), 13.4, 13.3 (Me$^{3,3'}$), 10.9, 10.4 (Me$^{5,5'}$), 8.9 (AlCH$_2$CH$_3$), 1.0 (AlCH$_2$CH$_3$), 150.5−128.0 (*Ph*$_3$CCH$_2$CH$_3$), 53.2 (Ph$_3$CCH$_2$CH$_3$), 31.0 (Ph$_3$CCH$_2$CH$_3$), 9.1 (Ph$_3$CCH$_2$CH$_3$). 148.8−121.0 (B(*C*$_6$F$_5$)$_4$). ^{19}F NMR (THF-d_8, 297 K; δ (ppm)): −133.1 (d, $^3J_{F-F}$ = 16.8 Hz, 2F, *o*-C$_6$F$_5$), −163.9 (t, $^3J_{F-F}$ = 18.3 Hz, 1F, *p*-C $_6$F$_5$), −169.7 (t, $^3J_{F-F}$ = 17.2 Hz, 2F, *m*-C $_6$F$_5$).

Synthesis of 17. In a glovebox, equimolar amounts of [AlEt$_2${κ^2-(*S*)-mbpam}] (**10**; 0.057 g, 0.13 mmol) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.12 g, 0.13 mmol) were added to a sample vial and dissolved in 0.6 mL of THF-d_8. The resulting pale yellow solution was transferred to an NMR tube (10 mm o.d.) and analyzed. ^{1}H NMR (THF-d_8, 297 K; δ (ppm)): 7.40−7.00 (NCH(CH$_3$)*Ph*), 7.05 (s, 1H, CH), 6.22, 6.12 (s, 2H, H$^{4,4'}$), 5.30 (m, $^3J_{H-H}$ = 6.9 Hz, 1H, NC*H*(CH$_3$)Ph), 1.60 (d, $^3J_{H-H}$ = 7.9 Hz, 3H, NCH(C*H*$_3$)Ph), 2.38, 2.20 (s, 6H, Me$^{5,5'}$), 2.30, 2.25 (s, 6H, Me$^{3,3'}$), 0.92 (s, $^3J_{H-H}$ = 7.9 Hz, 3H, AlCH$_2$C*H*$_3$), 0.03 (m, $^3J_{H-H}$ = 7.9 Hz, 2H, AlC*H*$_2$CH$_3$), 7.40−7.00 (Ph$_3$CCH$_2$CH$_3$), 2.55 (m, 2H, Ph$_3$CC *H*$_2$CH$_3$), 0.85 (t, $^3J_{H-H}$ = 6.9 Hz, 3H, Ph$_3$CCH$_2$C*H* $_3$). ^{13}C{^{1}H} NMR (THF-*d* $_8$, 297 K; δ (ppm)): 157.4 (N*C*═O), 151.2, 149.3, 147.5, 139.3, 137.3 (C$^{3,3\text{ or }5,5'}$, C^{ipso} NCH(CH$_3$)Ph), 128.3 (C^m NCH(CH$_3$)Ph), 127.3 (C^o NCH(CH$_3$)Ph), 126.4 (C^p NCH(CH$_3$)Ph), 54.1 (N*C*H(CH$_3$)Ph), 21.7 (NCH(*C*H$_3$)Ph), 110.1, 109.8 (C$^{4,4'}$), 69.1 (CH), 14.4, 14.1 (Me$^{3,3'}$), 12.2, 11.8 (Me$^{5,5'}$), 10.6 (AlCH$_2$CH$_3$), 0.6 (AlCH$_2$CH$_3$), 150.5−128.0 (*Ph*$_3$CCH$_2$CH$_3$), 51.6 (Ph$_3$CCH$_2$CH$_3$), 28.9 (Ph$_3$CCH$_2$CH$_3$), 8.2 (Ph$_3$CCH$_2$CH$_3$), 146.8−120.0 (B(*C*$_6$F$_5$)$_4$). ^{19}F NMR (THF-d_8, 297 K; δ (ppm)): −133.8 (d, $^3J_{F-F}$ = 16.2 Hz, 2F, *o*-C$_6$F$_5$), −163.4 (t, $^3J_{F-F}$ = 18.2 Hz, 1F, *p*-C$_6$F$_5$), −169.3 (t, $^3J_{F-F}$ = 17.8 Hz, 2F, *m*-C$_6$F$_5$).

General Procedure for Solution Polymerization of ε-Caprolactone, L-LA, and *rac*-LA. Polymerizations of ε-caprolactone (CL) were carried out on a Schlenk line in a flame-dried round-bottomed flask equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent and temperature equilibration was ensured by stirring the solution for 15 min in a temperature-controlled bath. ε-CL was injected, and polymerization times were measured from that point. Polymerizations were terminated by the addition of acetic acid (5 vol %) in methanol. Polymers were precipitated in methanol, filtered off, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight. Polymerizations of L-lactide and *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried Schlenk tube equipped with a magnetic stirrer. The Schlenk tubes were charged in the glovebox with the required amount of *rac*-lactide and initiator, separately, and then attached to the vacuum line. The initiator and monomer were dissolved in the appropriate amount of solvent, and temperature equilibration was ensured in both Schlenk flasks by stirring the solutions for 15 min in a bath. Polymerizations were stopped by injecting a solution of acetic acid (5 vol %) in methanol. Polymers were precipitated in methanol, filtered off, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

General Procedure for Solvent-Free (Melt) Polymerization of *rac*-LA. A Schlenk flask was charged with catalyst and *rac*-LA in the desired ratio and heated to 130 °C for 9 min with stirring. The mixture was cooled to room temperature, wet acidic THF (10 mL) was added, and the resulting solution was evaporated to dryness to give the crude polymer.

X-ray Crystallographic Structure Determination. Yellow (for **1** and **2**) and colorless (**7**) crystals were obtained by diffusion of toluene/hexane. X-ray data for **1**, **2**, and **7** were collected on a Bruker X8 APEX II CCD area detector diffractometer at T = 180 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å, sealed X-ray tube). Data were integrated using SAINT,[32] and an absorption correction was performed with the program SADABS.[33] The structures were solved by direct methods using SHELXTL[34] and refined by full-matrix least-squares methods based on F^2. Non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were placed in calculated positions and thereafter treated as riding. Salient crystallographic data are summarized in Table 2, and further details can be found in the Supporting Information in CIF format. Selected geometric data are presented in Table 3. For compound **1**, only crystals of low quality could be grown. Because of the weak diffraction, reflections have been included only up to θ = 22.0° for the refinement; however, the data were of sufficient quality to determine the molecular and crystal structure. The asymmetric unit contains two independent molecules. In the crystal structure of compound **7**, the acetamidate and ethyl groups are disordered over two positions and were modeled as a 50:50 isotropic mixture.

■ ASSOCIATED CONTENT

Supporting Information. Text, figures, tables and CIF files giving VT NMR analyses and kinetic parameters carried out for complexes **1**−**10** (from +40 to −80 °C) and details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for complexes **1**, **2**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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