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Syntheses and Reactions of Derivatives of (Pyrrolylaldiminato)germanium(II) and -Aluminum(III)

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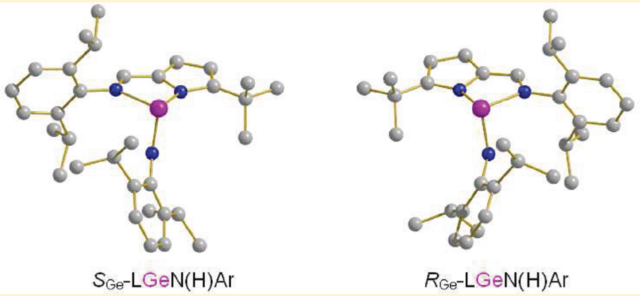
Ⓢ *Supporting Information*



ABSTRACT: (Pyrrolylaldiminato)germanium(II) chloride, LGeCl (**1**), was prepared by reacting LLi (L = 2-(ArN=CH)-5-*t*BuC_4H_2N; Ar = 2,6-*i*$Pr_2C_6H_3$) with 1 equiv of $GeCl_2$·(dioxane). Treatment of LGeCl (**1**) with KO*t*Bu or LiN(H)Ar yielded LGeR (R = O*t*Bu (**2**), N(H)Ar (**3**)) by halide metathesis. (Pyrrolylaldiminato)methylaluminum chloride, LAlMe(Cl) (**4**), was obtained from the reaction of LLi and $MeAlCl_2$ or by treating LH with Me_2AlCl in toluene. Treatment of LH with Me_2AlCl or $AlCl_3$ in Et_2O at −18 °C resulted in the 1:1 adducts LH·$AlMe_2Cl$ (**5**) and LH·$AlCl_3$ (**5′**), respectively. Further reaction of **4** with 2 equiv of $LiNEt_2$ led to the insertion of the NEt_2 group into the C=N bond together with the elimination of LiCl, to afford L′(NEt_2)AlMe(NEt_2)Li(THF) (**6**). Similarly, treatment of **4** with 2 equiv of $LiPPh_2(THF)_2$ gave L′(PPh_2)AlMe(OC_4H_8-PPh_2)$Li(THF)_2$ (**7**) accompanied by ring opening of THF. Single-crystal X-ray structure determinations revealed that **3** and **4** each contained enantiomeric pairs, while **6** and **7** each adopted a single enantiomer.

INTRODUCTION

Monoanionic bidentate nitrogen ligands are of particular interest in stabilizing well-defined complexes with low-valent or low-coordinate metal centers for the intriguing significance of structure and reactivity. Representative examples are β-diketiminato,[1] amidinato,[2] guanidinato,[3] and aminotroponiminato[4] derivatives with advantageous feasibility in steric and electronic modification of their auxiliary substituents to serve as spectator ligands. In contrast, pyrrolylaldiminato ligands,[5] which have a close resemblance to the salicylaldiminato stereotype,[6] have been less explored. Nevertheless, increasing attention is being paid to the synthesis and application of pyrrolylaldiminato complexes by virtue of their versatility in bonding modes.[7,8] Moreover, they are used in the polymerization of ethylene,[9−11] norbornene,[12] and methyl methacrylate,[13] as well as in copolymerization of methyl acrylate and olefins[14] and oligomerization of ethylene.[15] In this regard, we have reported the synthesis of pyrrolylaldiminato complexes of Zn, Mg, and Al.[16] In terms of their structural features it was noticed that most of the bis(pyrrolylaldiminato) complexes are chiral. To our surprise, studies of the synthesis and reaction of heteroleptic mono(pyrrolylaldiminato) complexes containing mixed substituents are scarce. They might lead to interesting enantiomers. Some mono(pyrrolylaldiminato) systems of Ni(II)[12,15] and Pt(II)[17] exhibit cis/trans arrangement in a square-planar conformation. In continuation of our research interest, we describe herein the preparation and characterization of LGeCl (**1**) and LAlMe(Cl) (**4**) stabilized by a pyrrolylaldiminato ligand (L = 2-(ArN=CH)-5-*t*BuC_4H_2N; Ar = 2,6-*i*$Pr_2C_6H_3$). Further derivatives were obtained through metathesis with lithium or potassium reagents.

RESULTS AND DISCUSSION

Reaction of LLi (L = 2-(ArN=CH)-5-*t*BuC_4H_2N; Ar = 2,6-*i*$Pr_2C_6H_3$) with 1 equiv of $GeCl_2$·(dioxane) in Et_2O resulted in the facile elimination of LiCl and formation of the pyrrolylaldiminato chlorogermylene LGeCl (**1**; Scheme 1) as a pale yellow solid in moderate yield. In the ^1H NMR spectrum of **1** in C_6D_6, characteristic isopropyl patterns of two sets of septets for methylene groups (3.12, 3.57 ppm) and four sets of doublets for methyl groups (0.91−1.34 ppm) are observed due to the asymmetric conformation with restricted rotation. This result is in sharp contrast to the one septet and one doublet pattern observed for LNa(THF).[18] A high-field singlet (1.38 ppm) is assigned to the *t*Bu group. A recent example of enantiomeric chlorogermylene was reported using a bis(oxazoline) ligand.[19] Further treatment of LGeCl (**1**) with KO*t*Bu and LiN(H)Ar resulted in the isolation of LGeO*t*Bu (**2**) and LGeN(H)Ar (**3**), respectively, by elimination of alkali-metal chloride. The ^1H NMR spectrum of LGeO*t*Bu (**2**) displays a pattern similar to that of LGeCl (**1**) with respect to

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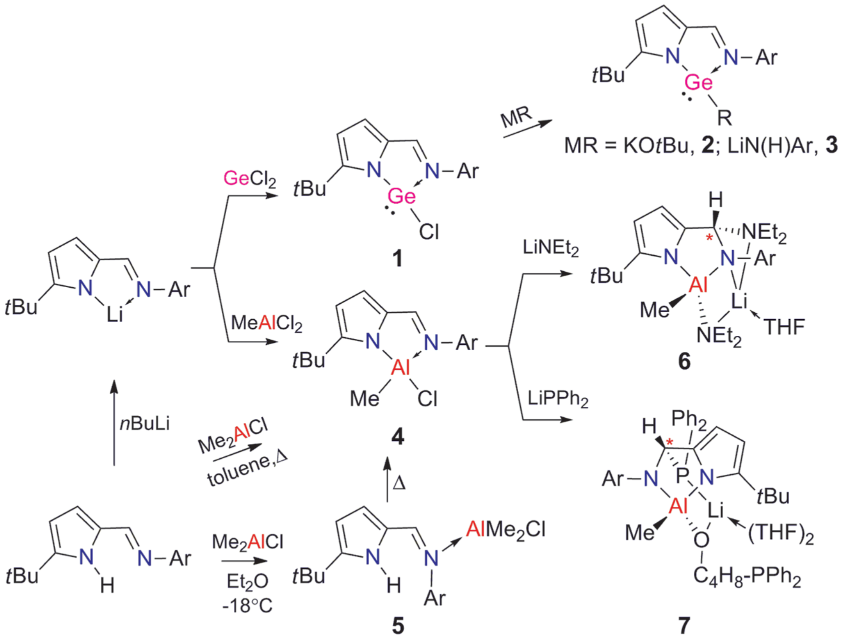
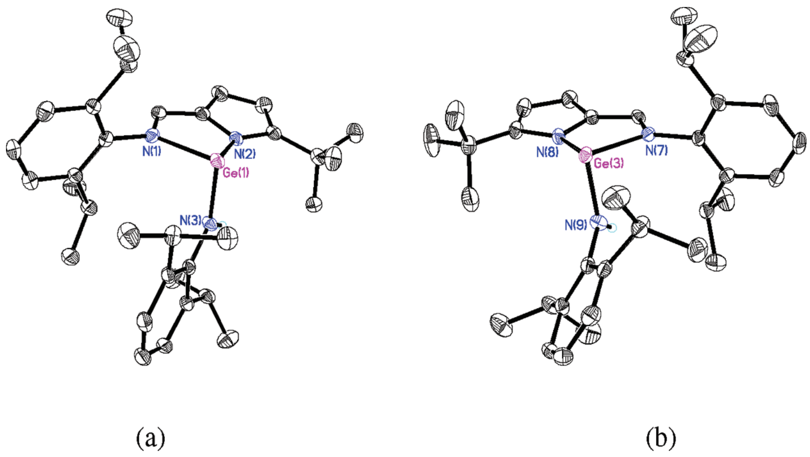
Scheme 1. Formation of Compounds 1−7 (Ar = 2,6-iPr$_2$C$_6$H$_3$)





(a) (b)

Figure 1. Molecular structures of the (a) S_{Ge} and (b) R_{Ge} forms of LGeN(H)Ar (**3**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except those of the amine group, are omitted for clarity. Selected bond lengths (Å) and angles (deg): S_{Ge}, Ge(1)−N(1) = 2.104(4), Ge(1)−N(2) = 2.006(4), Ge(1)−N(3) = 1.885(4), N(1)−Ge(1)−N(2) = 79.26(16), N(1)−Ge(1)−N(3) = 92.48(18), N(2)−Ge(1)−N(3) = 93.93(17); R_{Ge}, Ge(3)−N(7) = 2.071(4), Ge(3)−N(8) = 2.008(4), Ge(3)−N(9) = 1.890(4), N(7)−Ge(3)−N(8) = 79.58(15), N(7)−Ge(3)−N(9) = 90.91(16), N(8)−Ge(3)−N(9) = 98.11(16).

the isopropyl resonances, but an additional singlet (1.48 ppm) is assignable to the OtBu group, with the expected integral ratios relative to those of the ligand backbone. In the ^{1}H NMR spectrum of LGeN(H)Ar (**3**) three sets of septets are observed, which are due to the pyrrolylaldiminato ligand (3.31, 3.42 ppm) and the arylamido substituent (3.11 ppm). The amido proton resonance appears at 4.70 ppm, which is consistent with the presence of a NH stretching absorption in the IR spectrum (3399 cm^{-1}).

Compounds LGeCl (**1**) and LGeOtBu (**2**) are readily soluble in common organic solvents, and it is difficult to form crystals of good quality. Crystals of LGeN(H)Ar (**3**) suitable for single-crystal X-ray structural analysis were obtained from a concentrated n-hexane solution. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **3** is depicted in Figure 1, and crystal data and collection parameters are given in Table S1 (see the Supporting Information). There are four crystallographically independent molecules per unit cell. Three molecules can be described as having a S_{Ge} configuration (Figure 1a), and the other one can be treated as their enantiomer (R_{Ge}; Figure 1b).[20] The Ge centers are all three-coordinate, and each displays a pyramidal geometry, while corresponding bond lengths and angles of discrete molecules are highly comparable to each other. The terminal Ge−N distances (1.885(4), 1.890(4) Å) are noticeably shorter than those of the corresponding endocyclic pairs (2.006(4)−2.104(4) Å). This observation is consistent with the previous study of the β-diketiminato analogue ^{iPr}LGeN(H)Ar (^{iPr}L = CH[C(Me)N(Ar)]$_2$).[21]

Treatment of LLi with 1 equiv of MeAlCl$_2$ in Et$_2$O resulted in the formation of (pyrrolylaldiminato)methylaluminum chloride, LAlMe(Cl) (**4**; Scheme 1), in modest yield. The ^{1}H NMR spectrum of **4** features the isopropyl resonances as two septets (3.03, 3.58 ppm) and four doublets (0.88−1.34 ppm).

This is in marked contrast to the one septet and two doublets pattern observed for $LAlCl_2$ or $LAlMe_2$.[16,18] The high-field singlet (−0.13 ppm) is due to a methyl group at the Al site with correct integral ratio, which is shifted slightly downfield in comparison with that of $LAlMe_2$ (−0.23 ppm).[16,18] Compound **4** crystallizes in the orthorhombic space group $Pna2_1$ (Table S1, Supporting Information). The distorted-tetrahedral Al center is surrounded by one methyl group, one chlorine, and two nitrogen atoms. R_{Al}-**4** (Figure 2) and S_{Al}-**4** (Figure S1, Supporting Information) share the same ligand skeleton in a ratio of 2:1. The Al−C (1.819(2), 1.833(6) Å) and Al−Cl (2.0911(9), 2.0607(14) Å) bond lengths are correspondingly shorter than those observed in $LAlMe_2$ (1.950(7) Å) and $LAlCl_2$ (2.111(2) Å).[18]

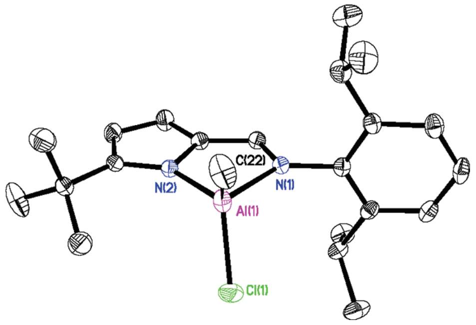


Figure 2. Molecular structure of LAlMe(Cl) (R_{Al}-**4**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 1.9440(11), Al(1)−N(2) = 1.9053(11), Al(1)−C(22) = 1.819(2), Al(1)−Cl(1) = 2.0911(9); N(1)−Al(1)−N(2) = 86.56(5), N(1)−Al(1)−C(22) = 113.46(11), N(2)−Al(1)−C(22) = 117.52(10), N(1)−Al(1)−Cl(1) = 109.71(4), N(2)−Al(1)−Cl(1) = 116.08(4), C(22)−Al(1)−Cl(1) = 111.09(11).

To modify the preparation of LAlMe(Cl) (**4**), an alternative route was explored by intermolecular elimination of methane from the ligand (LH) and metal alkyls (Me_2AlCl). When this reaction was first carried out in a small amount of Et_2O at −18 °C, no precipitate or gas evolution was observed. After the solution was stored at −18 °C for 2 days in a freezer, a colorless crystalline solid was obtained. According to the spectroscopic study, it turned out to be the 1:1 adduct of $LH{\cdot}AlMe_2Cl$ (**5**) instead of the initially targeted LAlMe(Cl) (**4**). In the IR spectrum of **5**, the NH stretching frequency is found at 3424 cm^{-1}, corresponding to the singlet for the NH proton resonance (8.49 ppm) in the ^1H NMR spectrum. Furthermore, the ^1H NMR spectrum also exhibits a singlet (−0.14 ppm) due to the $AlMe_2$ group with expected integral ratio. The formation of **5** was further documented by single-crystal X-ray structural analysis (Figure S2, Supporting Information). Compound **5** crystallizes in the monoclinic space group $P2_1/c$, containing an open chain like ligand, together with a slightly distorted tetrahedral geometry around the aluminum center completed by one nitrogen, one chlorine, and two methyl carbon atoms. The short N(1)−C(1) bond length (1.290(5) Å) supports the double-bond character, which is shorter in comparison with that of the free pyrrolylaldiminato ligand stabilized nickel complex (1.307(5) Å).[8] The NH functionality is arranged cis to the Ar group relative to the C(1)−C(2) bond. Compound **5** is stable in the solid state or in Et_2O solution at room temperature but gradually degraded to LAlMe(Cl) (**4**) in toluene at elevated temperatures. Consequently, the same reaction of LH with Me_2AlCl conducted in toluene under reflux for 2 h afforded LAlMe(Cl) (**4**) in high yield, by cleaving one of the Al−C bonds with elimination of methane. The comparable adduct $LH{\cdot}AlCl_3$ (**5′**) was also available from LH and $AlCl_3$ in Et_2O at −18 °C. In sharp contrast to that of **5**, the X-ray analysis of **5′** reveals that the NH functionality and the Ar group adopt a trans arrangement (Figure S3, Supporting Information).

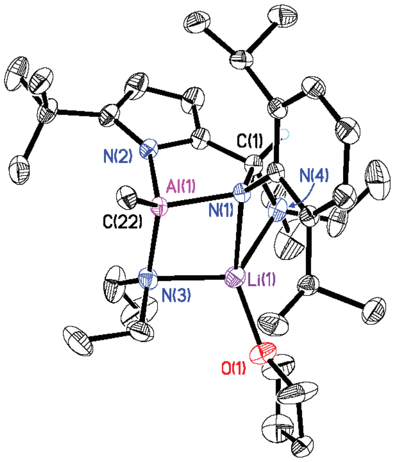


Figure 3. Molecular structure of $L'(NEt_2)AlMe(NEt_2)Li(THF)$ (**6**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except that of C(1), are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 1.9023(19), Al(1)−N(2) = 1.895(2), Al(1)−N(3) = 1.879(2), Al(1)−C(22) = 1.960(2), Al(1)···Li(1) = 2.781(4), N(1)−Li(1) = 2.352(5), N(3)−Li(1) = 2.101(5), N(4)−Li(1) = 2.086(5), C(1)···Li(1) = 2.656(5), O(1)−Li(1) = 1.978(5); N(1)−Al(1)−N(2) = 89.54(9), N(3)−Al(1)−C(22) = 117.03(11), N(1)−Al(1)−C(22) = 110.95(9), N(2)−Al(1)−C(22) = 122.29(10).

An equimolar reaction of LAlMe(Cl) (**4**) with $LiNEt_2$ monitored with NMR spectroscopy indicated a partial (nearly half) conversion of **4** into a new compound. Accordingly, the reaction of LAlMe(Cl) (**4**) with 2 equiv of $LiNEt_2$ was carried out in THF on a preparative scale. From the concentrated *n*-hexane extract a colorless crystalline solid of **6** was obtained. An initial ^1H NMR spectroscopic study of **6** reveals a upfield shift of the AlMe proton resonance (−0.33 ppm) relative to that of the precursor **4** (−0.13 ppm). Furthermore, a singlet emerges at 4.87 ppm, which may imply a change other than a simple metathesis process is involved in this reaction. The structure of $L'(NEt_2)AlMe(NEt_2)Li(THF)$ (**6**) was established by single-crystal X-ray crystallography (Figure 3). Compound **6** crystallizes in the monoclinic space group $P2_1/c$. To our surprise, **6** contains two NEt_2 groups. One is bound to the Al center, and the other is inserted into the C═N bond of the ligand. It has been previously reported that the C═N moiety can undergo alkylation or reduction to result in an amido-type ligand. For example, an intramolecular benzylation of the imino function of a (pyrrolylaldiminato)zirconium complex resulted in an amidopyrrolyl complex,[11] while the reduction of one imino moiety of a bis(imino)pyrrolyl ligand of a lutetium complex with BH_4^- generated a complex with both imino and amido functionalities.[22] In the current case, the pyrrolylaldiminato ligand degraded to a dianionic amidopyrrolyl ligand, denoted as $L'(NEt_2)$, so that compound **6** can be regarded as a 1:1 adduct of the neutral $L'(NEt_2)AlMe$ and $LiNEt_2(THF)$. To accommodate the latter, the former acts both as a Lewis base through its N sites and as a Lewis acid through its Al site. This could be the driving force to allow the reactions of NEt_2 insertion and $LiNEt_2$ inclusion under very mild conditions. This is in sharp contrast to the metathesis reactions in the case of LGeCl (**1**) and its derivatives. It is noticeable that in the core structure of **6** those atoms that concomitantly form two distorted four-membered Al(1)−N(3)−Li(1)−N(1) and N(1)−Li(1)−N(4)−C(1) rings are all of tetrahedral geometry. The coordination sphere of Al(1) is completed by three nitrogen atoms and one methyl carbon atom, while Li(1) is supported by three nitrogen atoms and one THF molecule. According to the orientation of the Al−C bond relative to the ligand backbone, it is suggested that the absolute configuration of the parent R_{Al}-**4** is retained in **6**. Moreover, the C(1) atom forms a new chiral center adopting the *R* configuration. The Al(1)−C(22) distance (1.960(2) Å) of **6** is relatively longer than those observed in **4**. The nonplanar Al(1)−N(3)−Li(1)−N(1) core has long Li−N (2.101(5), 2.352(5) Å) and short Al−N (1.879(2), 1.9023(19) Å) edges, which are consistent with those observed in $Me_2Al[(PhCH_2)_2N]_2Li(THF)$ (2.09 vs 1.912 Å).[23]

In a similar route, treatment of LAlMe(Cl) (**4**) with 2 equiv of $LiPPh_2(THF)_2$ in toluene resulted in the formation of **7**. In the ^1H NMR spectrum, the AlMe proton resonance (−0.22 ppm) is found shifted moderately upfield in comparison with that of precursor **4** (−0.13 ppm). The ^{31}P NMR spectrum shows two resonances (−17.12, −40.74 ppm), indicating different bonding modes of the phosphorus centers. The structure of compound **7** ($L'(PPh_2)AlMe(OC_4H_8\text{-}PPh_2)Li(THF)_2$) was studied by single-crystal X-ray structural analysis (Figure 4). Compound **7** crystallizes in the triclinic space group $P\bar{1}$. Two PPh_2 groups are involved in this compound; one is (as expected) to be inserted into the C═N moiety, while the other is bound to the metal centers through a ring-opened THF molecule. An analogous insertion of ring-opened THF into the M−P bond was previously demonstrated when $^{iPr}LYI_2(THF)$ was treated with $[KP(H)Ar^*(THF)]_2$ (Ar^* = 2,6-(2,4,6-$i\mathrm{Pr}_3C_6H_2)_2C_6H_3$).[24] The Al(1) atom of **7** is surrounded by one methyl carbon, two nitrogens, and one oxygen atom. The Al(1)−C(22) bond length (1.938(7) Å) is slightly shorter relative to that of **6**, while the Al(1)−O(1) distance (1.775(5) Å) is marginally longer than those in $[Me_2AlN(2\text{-}C_5H_4N)\text{-}Ph]_2(O)Li_2(THF)_2$ (1.746(5), 1.763(5) Å).[25] In contrast to **6**, there are no intramolecular short contacts observed between Li and N/C atoms in **7**. In compensation, the $LiOC_4H_8\text{-}PPh_2$ fragment is solvated by two THF molecules, and the Li^+ cation is coordinated by the phosphorus atom at C(1) to complete the distorted-tetrahedral geometry. This arrangement generates an AlOLiPCN six-membered heterocycle, sharing the C(1)−Al(1) and Al(1)−N(1) edges with the contiguous C_2N_2Al ring. The chiral C(1) atom adopts the *R* configuration, while Al(1) follows the configuration of precursor S_{Al}-**4**, as indicated by the projecting direction of the Al−C linkage. Likewise, compound **7** can be viewed as a 1:1 adduct of the neutral $L'(PPh_2)AlMe$ and $LiOC_4H_8\text{-}PPh_2(THF)_2$. Since R_{Al}-**4** is the major component in the starting material, the exclusive formation of **7** with inherited S_{Al} configuration may imply a flexible Al−methyl inversion occurring via the possible intermediate $L'(PPh_2)AlMe$ with a quasi-planar geometry around Al.[26]

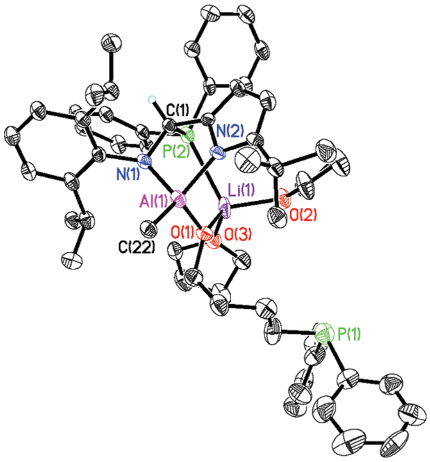


Figure 4. Molecular structure of $L'(PPh_2)AlMe(OC_4H_8\text{-}PPh_2)Li(THF)_2$ (**7**). Thermal ellipsoids are drawn at the 50% level, and all hydrogen atoms, except that of C(1), are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−N(1) = 1.861(6), Al(1)−N(2) = 1.898(5), Al(1)−C(22) = 1.938(7), Al(1)−O(1) = 1.775(5), Al(1)···Li(1) = 3.163(13), P(2)−Li(1) = 2.722(15); N(1)−Al(1)−N(2) = 88.6(2), O(1)−Al(1)−C(22) = 114.2(3), N(1)−Al(1)−C(22) = 114.4(3), N(2)−Al(1)−C(22) = 121.2(3).

In both **6** and **7** each methyl group on Al is oriented trans with respect to the inserted R group (R = NEt_2, PPh_2) at the chiral C(1) site. It is therefore suggested that the formation of R_{Al}-**6** and S_{Al}-**7** is exclusively determined by the absolute configuration of C(1) (Schemes S1 and S2, Supporting Information). The preferred formation of the *R* configuration at C(1) might be due to stereoselective reasons.

■ CONCLUSION

The novel pyrrolylaldiminato chlorogermylene LGeCl (**1**) and methylaluminum chloride LAlMe(Cl) (**4**) have been prepared and shown to be useful precursors for metathesis reactions. The pyrrolylaldiminato ligand has several distinct features. First, it can act as a neutral ligand to stabilize a chemically active species such as dimethylaluminum chloride to form the 1:1 adduct $LH\cdot AlMe_2Cl$ (**5**) under mild conditions. Second, its asymmetric character gives rise to enantiomerism in the derived complexes, as observed in the single-crystal X-ray structural analysis of LGeN(H)Ar (**3**) and LAlMe(Cl) (**4**), respectively. Third, the R group from aluminum can be inserted into the C═N bond of the ligand L, which results in interesting complexes such as $L'(NEt_2)AlMe(NEt_2)Li(THF)$ (**6**) and $L'(PPh_2)AlMe(OC_4H_8\text{-}PPh_2)Li(THF)_2$ (**7**). Compound **6** as well as **7** adopts a single enantiomer due to the preferential formation of the *R* configuration at the newly created chiral carbon center.

■ EXPERIMENTAL SECTION

Materials and Methods. All manipulations were carried out under nitrogen by using Schlenk techniques or inside a MBraun glovebox filled with argon, in which the calibrated values of O_2 and H_2O were controlled below 1.2 ppm. Organic solvents, including toluene, *n*-hexane, THF, and Et_2O, were predried with sodium wire and then heated with sodium/potassium benzophenone under nitrogen prior to use. C_6D_6 was degassed, dried with sodium/potassium alloy, and filtered before use. NMR spectra were recorded on a Bruker AV 500 spectrometer. Melting points were measured in a sealed glass tube using a Büchi B-540 instrument without correction. IR spectra were recorded on a Nicolet 380 (Thermo Fisher Scientific) spectrometer. Elemental analysis was performed with a Thermo Quest Italia SPA EA 1110 instrument. Chemicals commercially available were purchased from Aldrich and used as received. LH (L = 2-(ArN═CH)-5-tBuC_4H_2N; Ar = 2,6-$i\mathrm{Pr}_2C_6H_3$),[10] $GeCl_2\cdot(dioxane)$,[27]

$LiPPh_2(THF)_2$,[28] $LiNEt_2$, and LiN(H)Ar[29] were prepared as described in the literature or by modified methods.

LGeCl (1). At −18 °C *n*BuLi (0.42 mL, 2.4 M, 1 mmol) was added drop by drop to a solution of LH (0.310 g, 1 mmol) in Et_2O (30 mL). The mixture was stirred and warmed to room temperature. Additional stirring for 12 h ensured complete formation of LLi. To a solution of $GeCl_2$·(dioxane) (0.232 g, 1 mmol) in Et_2O (20 mL) was added the above solution of LLi at −18 °C. After stirring for another 12 h at room temperature, the formed precipitate was filtered off and the solvent was removed in vacuo. The residue was treated upon quick washing with cold *n*-hexane (2 × 2 mL) and then dried under vacuum to afford a pale yellow solid (0.26 g, 62%). Mp: 107 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.35 (s, 1H, C*H*═N), 7.00–7.12 (m, 3H, *Ar*), 6.76 (d, *J* = 3.9 Hz, 1H, pyrrole C*H*), 6.26 (d, *J* = 3.9 Hz, 1H, pyrrole C*H*), 3.57 (septet, 1H, C*H*Me_2), 3.12 (septet, 1H, C*H*Me_2), 1.38 (s, 9H, C*Me*$_3$), 1.34 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 1.12 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.00 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 0.91 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 163.80 (*Ar*), 155.59 (CH═N), 144.81, 143.06, 138.64, 135.39, 124.86, 123.45 (*Ar*), 122.54, 113.39 (pyrrole CH), 33.50 (CMe_3), 30.66 (C*Me*$_3$), 29.32, 28.03 ($CHMe_2$), 25.77, 24.42, 24.18, 23.91 (CH*Me*$_2$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1627 (m), 1592.72 (m), 1574.94 (vs), 1266.51 (s), 1231.34 (s), 1179.89 (m), 1099.65 (m), 1056.1 (s), 960.49 (m), 933.1 (m), 896.02 (m), 801.85 (m), 769.76 (m), 754.01 (m), 650.69 (w), 570.18 (w). Anal. Calcd for $C_{21}H_{29}ClGeN_2$ (417.6): C, 60.4; H, 7.00; N, 6.71. Found: C, 61.72; H, 7.02; N, 6.58.

LGeO*t*Bu (2). To a solution of LGeCl (0.418 g, 1 mmol) in Et_2O (30 mL) was added a suspension of KO*t*Bu (0.112 g, 1 mmol) in Et_2O at −18 °C with rigorous stirring. The reaction mixture was slowly warmed to room temperature and stirred for an additional 12 h. After filtration, the solvent was removed in vacuo to leave an oily paste. The residue was extracted with a small portion of *n*-hexane (5 mL) and then dried again under vacuum overnight to afford a light yellow solid (0.31 g, 68%). Mp: 78 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.51 (s, 1H, C*H*═N), 7.00–7.11 (m, 3H, *Ar*), 6.82 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 6.37 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 3.53 (septet, 1H, C*H*Me_2), 3.32 (septet, 1H, C*H*Me_2), 1.48 (s, 9H, OC*Me*$_3$), 1.34 (s, 9H, C*Me*$_3$), 1.26 (d, *J* = 6.6 Hz, 3H, CH*Me*$_2$), 1.19 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 0.96 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 0.88 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 161.59 (*Ar*), 154.82 (CH═N), 144.02, 142.87, 140.52, 135.16, 123.66, 123.44 (*Ar*), 120.10, 112.14 (pyrrole CH), 70.74 ($OCMe_3$), 33.53 (CMe_3), 33.43 (CMe_3), 30.46 (OC*Me*$_3$), 28.71, 27.57 ($CHMe_2$), 26.45, 24.52, 24.31, 23.56 (CH*Me*$_2$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1623.44 (vs), 1592.43 (vs), 1574.95 (vs), 1509.25 (vs), 1485.82 (vs), 1382.26 (vs), 1328.99 (s), 1298.8 (vs), 1268.21 (vs), 1232.98 (vs), 1181.89 (vs), 1106.02 (s), 1054.15 (vs), 1024.08 (s), 935.39 (vs), 892.73 (s), 858.22 (s), 800.73 (vs), 765.96 (vs), 754.34 (vs), 744.9 (s), 727.89 (s), 710.12 (s), 652.11 (s), 613.53 (vs), 567.46 (s). Anal. Calcd for $C_{25}H_{38}GeN_2O$ (455.2): C, 65.96; H, 8.41; N, 6.15. Found: C, 65.5; H, 8.51; N, 5.99.

LGeN(H)Ar (3). The preparation of **3** is similar to that of **2** using LiN(H)Ar (0.183 g, 1 mmol) and LGeCl (0.418 g, 1 mmol) as starting materials. Compound **3** was obtained as pale yellow crystals from *n*-hexane extract at −18 °C (0.40 g, 71%). Mp: 91 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.52 (s, 1H, C*H*═N), 7.00–7.12 (m, 6H, *Ar*), 6.81 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 6.36 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 4.70 (s, 1H, N*H*), 3.42 (septet, 1H, C*H*Me_2), 3.31 (septet, 1H, C*H*Me_2), 3.11 (septet, 2H, C*H*Me_2), 1.37 (s, 9H, C*Me*$_3$), 1.31 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.19 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.09 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.01 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 0.94 (d, *J* = 6.8 Hz, 3H, C*H*Me_2), 0.92 (d, *J* = 6.8 Hz, 3H, C*H*Me_2) ppm. ^{13}C NMR (126 MHz, C_6D_6): δ 161.62 (*Ar*), 154.39 (CH═N), 144.03, 143.37, 143.07, 140.51, 135.06, 134.84, 124.26, 123.43, 123.37 (*Ar*), 120.75 (pyrrole CH), 118.08 (*Ar*), 112.57 (pyrrole CH), 33.30 (CMe_3), 30.99 (C*Me*$_3$), 29.23 ($CHMe_2$), 29.02, 28.54 ($CHMe_2$), 24.50, 23.09 (CH*Me*$_2$), 26.03, 24.74, 23.41, 23.41 (CH*Me*$_2$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3399.42 (vw, −NH), 1593.51 (s), 1575.52 (vs), 1509.74 (m), 1335.28 (s), 1268.37 (s), 1231.75 (s), 1203.47 (m), 1178.45 (m), 1153.71 (m), 1108.15 (m), 1054.2 (vs), 1023.05 (m), 961.47 (w), 932.31 (m), 884.94 (m), 842.97 (m), 801.69 (m), 784.99 (w), 767.15 (s), 748.33 (s), 700.2 (w), 649.51 (vw), 566.5 (w), 462.44 (vw). Anal. Calcd for $C_{33}H_{47}GeN_3$ (558.4): C, 70.98; H, 8.48; N, 7.53. Found: C, 69.85; H, 8.43; N, 7.49.

LAlMe(Cl) (4). *Method a.* To a solution of in situ formed LLi (1 mmol) in Et_2O (30 mL) was added a solution of $MeAlCl_2$ (1 mL, 1.0 M, 1 mmol) at −18 °C with continuous stirring. The resulting mixture was slowly warmed to room temperature and stirred for 12 h. After workup, the LiCl precipitate was filtered off and the solvent was removed in vacuo to give an off-white solid. From the concentrated *n*-hexane extract at −18 °C, colorless crystals of **4** were obtained (0.22 g, 56%).

Method b. A mixture of LH (1.552 g, 5 mmol) and Me_2AlCl (5 mL, 1.0 M, 5 mmol) in toluene was heated under reflux for 2 h. After workup, the volatile components were removed under vacuum to afford a crystalline solid. From the concentrated *n*-hexane extract, crystals of **4** were afforded (1.76 g, 91%). Mp: 147 °C. ^1H NMR (500 MHz, C_6D_6): δ 7.36 (s, 1H, C*H*═N), 7.00–7.12 (m, 3H, *Ar*), 6.70 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 6.27 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 3.58 (septet, 1H, C*H*Me_2), 3.03 (septet, 1H, C*H*Me_2), 1.36 (s, 9H, C*Me*$_3$), 1.34 (d, *J* = 6.5 Hz, 3H, CH*Me*$_2$), 1.13 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 0.94 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 0.88 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), −0.13 (s, 3H, Al*Me*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 165.20 (*Ar*), 159.88 (CH═N), 144.41, 143.20, 139.36, 133.96, 124.52 (*Ar*), 124.41 (pyrrole CH), 123.68 (*Ar*), 113.63 (pyrrole CH), 33.53 (CMe_3), 30.58 (C*Me*$_3$), 28.20, 28.11 ($CHMe_2$), 25.54, 25.54, 23.35, 22.49 (CH*Me*$_2$), −6.1 (br, Al*Me*) ppm. ^{27}Al NMR (130 MHz, C_6D_6): δ 62.21 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1593.28 (m), 1573.69 (s), 1397.21 (w), 1326.38 (w), 1268.18 (m), 1233.47 (m), 1199.87 (w), 1186.91 (w), 1108.2 (vw), 1061.08 (s), 1031.65 (w), 933.8 (vw), 910.29 (w), 804.96 (w), 779.05 (w), 758.81 (w), 694.49 (vw), 664.08 (w), 572.57 (vw), 473.74 (w). Anal. Calcd for $C_{22}H_{32}AlClN_2$ (386.9): C, 68.29; H, 8.34; N, 7.24. Found: C, 67.94; H, 8.13; N, 7.08.

LH·AlMe$_2$Cl (5). To a solution of LH (0.310 g, 1 mmol) in Et_2O (5 mL) was added a solution of Me_2AlCl (1 mL, 1.0 M, 1 mmol) at −18 °C with stirring. The resulting mixture was stored at −18 °C in a freezer for 2 days. Colorless crystals of **5** were formed (0.19 g, 48%). Mp: 146 °C. ^1H NMR (500 MHz, C_6D_6): δ 8.49 (s, 1H, N*H*) 6.93–7.07 (br, 3H, *Ar*), 6.98 (s, 1H, C*H*═N), 6.19 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 5.56 (d, *J* = 3.8 Hz, 1H, pyrrole C*H*), 3.37 (septet, 2H, C*H*Me_2), 1.24 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.68 (d, *J* = 6.7 Hz, 6H, CH*Me*$_2$), 0.62 (s, 9H, C*Me*$_3$), −0.14 (s, 6H, Al*Me*) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 160.46, 156.45, 142.33 (*Ar*), 128.17 (CH═N), 125.02 (*Ar*), 129.07, 107.58 (pyrrole CH), 31.30 (CMe_3), 28.57 (C*Me*$_3$), 28.24 ($CHMe_2$), 23.61 (CH*Me*$_2$), −8.07 (br, Al*Me*) ppm. ^{27}Al NMR (130 MHz, C_6D_6): δ 61.48 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3424.18 (vw, NH), 1605.62 (w), 1584.16 (w), 1528.81 (w), 1258.68 (w), 1237.76 (w), 1186.47 (w), 1055.17 (w), 995.38 (w), 961.66 (w), 934.53 (vw), 895.05 (w), 807.85 (w), 785.41 (w), 675.19 (w), 569.17 (vw), 530.43 (vw), 470.15 (vw), 435.04 (vw). Anal. Calcd for $C_{23}H_{36}AlClN_2$ (403.0): C, 68.55; H, 9.00; N, 6.95. Found: C, 66.62; H, 8.84; N, 6.85.

LH·AlCl$_3$ (5′). The preparation of **5′** was carried out as for **5** using LH (0.310 g, 1 mmol) and $AlCl_3$ (0.133 g, 1 mmol) to afford a colorless crystalline solid (0.21 g, 48%). Mp: 208 °C. ^1H NMR (500 MHz, C_6D_6): δ 8.42 (s, 1H, N*H*), 6.96–7.06 (br, 3H, *Ar*), 6.98 (s, 1H, C*H*═N), 6.17 (m, 1H, pyrrole C*H*), 5.55 (m, 1H, pyrrole C*H*), 3.41 (septet, 2H, C*H*Me_2), 1.32 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.67 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.59 (s, 9H, C*Me*$_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 157.75, 156.79, 143.60 (*Ar*), 129.33 (CH═N), 125.43 (*Ar*), 132.59, 109.26 (pyrrole CH), 31.53 (CMe_3), 28.57 ($CHMe_2$), 28.33 (C*Me*$_3$), 23.76, 23.56 (CH*Me*$_2$) ppm. ^{27}Al NMR (130 MHz, C_6D_6): δ 61.79 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3361.64 (m, NH), 1600.64 (s), 1584.41 (s), 1417.07 (s), 1405.08 (s), 1262.97 (s), 1206.68 (m), 1098.26 (w), 1067.21 (m), 1028.68 (w), 988.36 (m), 963.98 (m), 915.61 (s), 819.21 (w), 804.64 (m), 796.15 (s), 781.73 (m), 695.25 (w), 653.83 (w), 549.95 (m), 530.04 (m), 495.93 (m), 438.12 (m), 417.52 (m). Anal. Calcd for $C_{21}H_{30}AlCl_3N_2$ (443.8): C, 56.83; H, 6.81; N, 6.31. Found: C, 57.01; H, 6.72; N, 6.45. Crystals of **5′** suitable for single-crystal X-ray analysis were grown from Et_2O solution.

L′(NEt$_2$)AlMe(NEt$_2$)Li(THF) (6). To a THF solution (40 mL) of LAlMe(Cl) (**4**; 0.387 g, 1 mmol) at −18 °C was added a solution of LiNEt$_2$ (0.158 g, 2 mmol) in THF (10 mL). The mixture was stirred for 12 h at room temperature, and all volatiles were removed in vacuo. From the concentrated Et$_2$O extract, a crystalline solid was obtained (0.41 g, 72%). Mp: 124 °C. ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.06−7.37 (m, *Ar*), 6.48 (d, *J* = 3.4 Hz, 1H, pyrrole C*H*), 6.26 (d, *J* = 3.0 Hz, 1H, pyrrole C*H*), 4.87 (s, 1H, C*H*N), 3.38 (m, 4H, O-C*H*$_2$ THF), 3.25 (q, *J* = 6.9 Hz, 2H, −C*H*$_2$CH$_3$), 3.02 (q, *J* = 6.9 Hz, 2H, −C*H*$_2$CH$_3$), 3.01 (septet, 1H, C*H*Me$_2$), 2.87 (q, *J* = 6.9 Hz, 4H, −C*H*$_2$CH$_3$), 2.58 (septet, 1H, C*H*Me$_2$), 1.63 (s, 9H, C*Me*$_3$), 1.37 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.35 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.26 (m, 4H, C*H*$_2$ THF), 1.23 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 1.15 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 0.93 (t, *J* = 6.9 Hz, 6H, −CH$_2$C*H*$_3$), 0.64 (t, *J* = 7.0 Hz, 6H, −CH$_2$C*H*$_3$), −0.32 (s, 3H, Al*Me*) ppm. ^{13}C NMR (126 MHz, C_6D_6): *δ* 159.47, 151.97, 146.50, 145.90, 141.56, 136.53, 125.88, 122.72, 122.28 (*Ar*), 107.41, 106.19 (pyrrole CH), 82.52 (CH−N), 68.34 (O−CH$_2$ THF), 42.89, 41.49 (CHMe$_2$), 40.47 (−CH$_2$CH$_3$), 32.71 (CMe$_3$), 31.79 (C*Me*$_3$), 28.44, 27.19 (−CH$_2$CH$_3$), 25.63, 25.97, 25.91, 24.61 (CH*Me*$_2$), 24.90 (CH$_2$ THF), 13.71 (−CH$_2$CH$_3$), −11.7 (br, Al*Me*) ppm.; ^{27}Al NMR (130 MHz, C_6D_6): *δ* 61.45 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1572.54 (vw), 1300.34 (m), 1283.99 (m), 1249.33 (w), 1232.67 (w), 1205.14 (w), 1181.2 (w), 1161.73 (w), 1139.81 (w), 1106.68 (w), 1073.83 (w), 1037.81 (w), 1002.74 (w), 941.74 (w), 894.3 (w), 872.7 (w), 799.75 (vw), 761.36 (w), 740.75 (w), 700.63 (vw), 660.58 (w), 618.73 (vw), 586.27 (vw), 511.1 (vw), 412.07 (w). Anal. Calcd for $C_{34}H_{60}AlLiN_4O$ (574.8): C, 71.05; H, 10.54; N, 9.75. Found: C, 70.26; H, 10.83; N, 9.68. Crystals of **6** suitable for single-crystal X-ray analysis were grown from *n*-hexane solution.

L′(PPh$_2$)AlMe(OC$_4$H$_8$-PPh$_2$)Li(THF)$_2$ (7). The preparation of **7** was similar to that of **6**, using LAlMe(Cl) (0.387 g, 1 mmol) and LiPPh$_2$(THF)$_2$ (0.673 g, 2 mmol) in toluene (0.54 g, 57%). Mp: 110 °C. ^{1}H NMR (500 MHz, C_6D_6): *δ* 7.48−6.87 (m, *Ar*/*Ph*), 6.10 (d, *J* = 3.0 Hz, 1H, pyrrole C*H*), 5.69 (d, *J* = 5.0 Hz, 1H, pyrrole C*H*), 5.10 (s, 1H, C*H*N), 3.90 (m, 2H, O−C*H*$_2$), 3.84 (septet, 1H, C*H*Me$_2$), 3.52 (septet, 1H, C*H*Me$_2$), 3.46 (m, 8H, O−C*H*$_2$ THF), 2.05 (m, 2H, P−C*H*$_2$), 1.80 (m, 2H, C*H*$_2$), 1.54 (s, 9H, C*Me*$_3$), 1.37 (m, 2H, C*H*$_2$), 1.35 (m, 8H, C*H*$_2$ THF), 1.33 (d, *J* = 6.7 Hz, 3H, CH*Me*$_2$), 1.21 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), 1.14 (d, *J* = 6.9 Hz, 3H, CH*Me*$_2$), 0.47 (d, *J* = 6.8 Hz, 3H, CH*Me*$_2$), −0.22 (s, 3H, Al*Me*) ppm; ^{13}C NMR (126 MHz, C_6D_6) *δ* 160.43 (Ar), 122.21−134.01 (*Ar*/*Ph*), 105.93, 64.73 (pyrrole CH), 103.96 (CH−N), 68.05 (O−CH$_2$-THF), 62.98 (O−CH$_2$), 35.99 (CH$_2$), 31.77 (CMe$_3$), 31.56 (C*Me*$_3$), 29.84 (CH$_2$), 28.34, 28.16 (P−CH$_2$), 27.63 (CHMe$_2$), 27.69, 25.94, 24.67, 22.11 (CH*Me*$_2$), 25.13 (CH$_2$-THF), 13.71 (−CH$_2$CH$_3$), −12.0 (br, Al*Me*) ppm. ^{27}Al NMR (130 MHz, C_6D_6): *δ* 62.38 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1596.79 (m), 1574.35 (s), 1305.88 (s), 1281.69 (s), 1232.82 (m), 1198.31 (m), 1183.3 (m), 1155.61 (m), 1069.86 (m), 1039.84 (s), 999.29 (m), 933.43 (w), 905.96 (m), 886.79 (m), 871.99 (w), 801.27 (w), 776.98 (w), 749.61 (s), 731.03 (s), 695.44 (s), 660.21 (m), 601.14 (vw), 569.51 (vw), 510.04 (w), 465.43 (w), 423.68 (w). Anal. Calcd for $C_{58}H_{76}AlLiN_2O_3P_2$ (945.1): C, 73.71; H, 8.11; N, 2.96. Found: C, 72.14; H, 7.80; N, 2.91. Crystals of **7**·0.5(*n*-hexane) suitable for single-crystal X-ray analysis were grown from *n*-hexane solution.

Structure Determination. X-ray crystallographic data were collected at 173 K on an Oxford Gemini S Ultra system (Cu K*α* radiation, *λ* = 1.541 78 Å, **3**; Mo K*α* radiation, *λ* = 0.710 73 Å, **5′**), a Rigaku R-AXIS RAPID Image Plate single-crystal diffractometer (Mo K*α* radiation, *λ* = 0.710 73 Å, **4**, **6**, and **7**), and a Bruker SMART CCD area-detector diffractometer (Mo K*α* radiation, *λ* = 0.710 73 Å) (**5**), respectively. Absorption corrections were applied using the spherical harmonics program (multiscan type). The structures were solved by direct methods (SHELXS-97)[30] and were refined by full-matrix least squares on F^2 with the SHELXL-97 program.[31] In general, the non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms unless otherwise specified.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Molecular structures of LAlMe(Cl) (S_{Al}-**4**, Figure S1), LH·AlMe$_2$Cl (**5**, Figure S2), and LH·AlCl$_3$ (**5′**, Figure S3), cell parameters, data collection, and structure solution and refinement details for compounds **3**−**7** (Table S1), and CIF file giving crystallographic data for **3**−**5**, **5′**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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