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Synthesis, Characterization, and Reaction of Aluminum Halide Amides Supported by a Bulky *β*-Diketiminato Ligand

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Monomeric aluminum chloride amides with the general formula $LAl(Cl)NR_2$ (**1**, R = Me; **2**, R = *i*Pr; **3**, R = $SiMe_3$; L = $HC[C(Me)N(Ar)]_2$; Ar = 2,6-$i$$Pr_2C_6H_3$) were prepared by selected routes. Treatment of $LAlBr_2$ (**4**) and $LAlI_2$ with $LiNMe_2$ yielded $LAl(Br)NMe_2$ (**5**) and $LAl(I)NMe_2$ (**6**), respectively. The alkylation of **1** and **2** with MeLi gave the corresponding methylated compounds $LAl(Me)NR_2$ (**7**, R = Me; **8**, R = *i*Pr); however, no reaction of **3** with MeLi was observed because of steric hindrance. Subsequent fluorination of **1**−**3** afforded $LAl(F)NR_2$ (**9**, R = Me; **10**, R = *i*Pr; **11**, R = $SiMe_3$). Compounds **1**–**11** were characterized by multinuclear NMR, electron impact mass spectrometry, and IR. The constitution of compounds **1**−**3** was confirmed by single-crystal X-ray diffraction studies.

Introduction

Aluminum amides have found widespread application as precursors for AlN materials[1] and are of interest in catalysis and organic synthesis.[2] Oligomeric nitrogen-rich compounds[3,4] or structurally characterized monomers[5–9] have been developed for this purpose. There are, however, only a few examples known of monomeric aluminum halide amides with two different substituents.[10] Nevertheless, several analogues are found in ytterbium-, samarium-, and scandium-containing compounds,[11–13] where the halogen can be eliminated by metathesis reactions, while in some cases of alkaline-earth metal and zinc amides,[14,15] it is the amido group that plays the role as a facile leaving group. These facts prompted us to prepare aluminum halide amides of the general formula $LAl(X)NR_2$ (L = ligand; X = halogen) and to explore their reactivity. Herein, we report on the synthesis and characterization of $LAl(X)NR_2$ (X = Cl, Br, I; R = Me, *i*Pr, $SiMe_3$; L = $HC[C(Me)N(Ar)]_2$; Ar = 2,6-$i$$Pr_2C_6H_3$).

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(1) (a) Bradley, D. C.; Frigo, D. M.; White, E. A. D. *Eur. Patent* 0331448, **1989**. (b) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *136*, 472–478. (c) Takahashi, Y.; Yamashita, K.; Motojima, S.; Sugiyama, K. *Surf. Sci.* **1979**, *86*, 238–245.

(2) (a) Rowley, C. N.; DiLabio, G. A.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 1983–1991. (b) Hoerter, J. M.; Otte, K. M.; Gellman, S. H.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 5177–5183.

(3) (a) Brask, J. K.; Chivers, T.; Yap, G. P. A. *Chem. Commun.* **1998**, 2543–2544. (b) Kovar, R. A.; Ashby, E. C. *Inorg. Chem.* **1971**, *10*, 893–899.

(4) Waggoner, K. M.; Olmstead, M. M.; Power, P. P. *Polyhedron* **1990**, *9*, 257–263.

(5) Jancik, V.; Pineda, L. W.; Pinkas, J.; Roesky, H. W.; Neculai, D.; Neculai, A. M.; Herbst-Irmer, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 2142–2145.

(6) Kenney, A. P.; Yap, G. P. A.; Richeson, D. S.; Barry, S. T. *Inorg. Chem.* **2005**, *44*, 2926–2933.

(7) Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Raston, C. L. *Inorg. Chem.* **1996**, *35*, 5696–5702.

(8) Atwood, D. A.; Rutherford, D. *Main Group Chem.* **1996**, *1*, 431–442.

(9) Zhu, H.; Yang, Z.; Magull, J.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 6420–6425.

(10) Chang, C. C.; Hsiung, C. S.; Su, H. L.; Srinivas, B.; Chiang, M. Y.; Lee, G. H.; Wang, Y. *Organometallics* **1998**, *17*, 1595–1601.

(11) Cui, C.; Shafir, A.; Schmidt, J. A. R.; Oliver, A. G.; Arnold, J. *Dalton Trans.* **2005**, 1387–1393.

(12) Chai, J.; Jancik, V.; Singh, S.; Zhu, H.; He, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hosmane, N. S. *J. Am. Chem. Soc.* **2005**, *127*, 7521–7528.

(13) Knight, L. K.; Piers, W. E.; Fleurat-Lessard, P.; Parvez, M.; McDonald, R. *Organometallics* **2004**, *23*, 2087–2094.

(14) (a) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 8738–8749. (b) Nembenna, S.; Roesky, H. W.; Mandal, S. K.; Oswald, R. B.; Pal, A.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2006**, *128*, 13056–13057. (c) Nembenna, S.; Roesky, H. W.; Nagendran, S.; Hofmeister, A.; Magull, J.; Wilbrandt, P. J.; Hahn, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 2512–2514.

(15) (a) Chisholm, M. H.; Gallucci, J.; Phomphrai, K. *Chem. Commun.* **2003**, 48–49. (b) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717–6725. (c) Avent, A. G.; Crimmin, M. R.; Hill, M. S.; Hitchcock, P. B. *Dalton Trans.* **2005**, 278–284.

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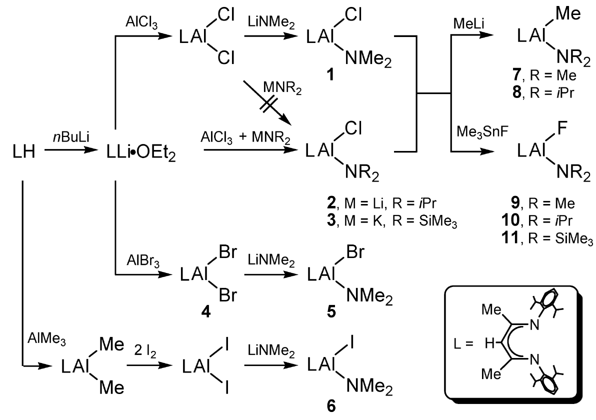
Scheme 1



Furthermore, the reactivity of these compounds was investigated toward alkylation, fluorination, and hydrolysis. All compounds were characterized by multinuclear NMR, IR, and electron impact mass spectrometry (EI-MS) measurements as well as by elemental analysis.

Results and Discussion

Synthesis of Chloride Derivatives 1–3. Aluminum amides are generally available under elimination of alkali halides, alkanes,[16] or hydrogen.[17,18] Using such a strategy, compound LAl(Cl)NMe$_2$ (**1**) was obtained in good yield by the reaction of LAlCl$_2$ with 1 equiv of LiNMe$_2$ in toluene (Scheme 1). The ^{1}H NMR spectrum of **1** displays one singlet (δ 2.64 ppm) corresponding to the methyl proton resonance of the NMe$_2$ group. The remaining resonances are attributed to the β-diketiminato ligand. In the mass spectrum, the most intense peak corresponds to the elimination of one methyl group and one amido group from the molecular ion.

The reaction of LAlCl$_2$ with LiN*i*Pr$_2$, however, led to a mixture of products, most of which were recognized as the starting material. We suggest that the steric bulk of the *i*Pr substituent prevents the metathesis at the Al atom. To overcome this difficulty, a one-pot strategy was proposed. The reaction of AlCl$_3$ and LiN*i*Pr$_2$ followed by the addition of 1 equiv of LLi·OEt$_2$ finally afforded the target product LAl(Cl)N*i*Pr$_2$ (**2**). The ^{1}H NMR spectrum of **2** exhibits one septet (δ 3.10 ppm) and one doublet (δ 0.84 ppm) representing the isopropyl methine and methyl proton resonances of the N*i*Pr$_2$ group, respectively. The base peak in the mass spectrum is assigned to the fragment [M$^+$ − N*i*Pr$_2$].

An attempt to react LAlCl$_2$ with the even more bulky MN(SiMe$_3$)$_2$ (M = Li, Na, K) was not successful either, although analogous reactions with Mes$_2$AlCl(THF),[8] LSmCl$_2$,[11] and LYbCl$_2$[12] have been reported. Then the above-mentioned one-pot strategy was tentatively employed to this system. When AlCl$_3$ and KN(SiMe$_3$)$_2$ are placed together in toluene, surprisingly an almost clear solution with only a small amount of insoluble material is formed. No precipitate was produced in this system even after stirring at room temperature for 1 week. To explain this, we postulate the formation of an intermediate of composition K[Cl$_3$AlN(SiMe$_3$)$_2$], which is soluble or finely dispersed in toluene and evidently stable with respect to KCl elimination at room temperature. Treatment of this intermediate with LLi·OEt$_2$ followed by filtration and purification resulted in the recovery of LAl(Cl)N(SiMe$_3$)$_2$ (**3**) as a colorless microcrystalline solid. The ^{1}H NMR spectrum of **3** shows two equally intense singlets (δ 0.30 and 0.42 ppm) for the N(SiMe$_3$)$_2$ group with corresponding resonances in the ^{29}Si NMR spectrum (δ −3.20 and +2.24 ppm). The mass spectrum confirms the composition with the base peak for the fragment [M$^+$ − Me].

In a previous contribution, we reported that the aluminum diamide LAl(NH$_2$)$_2$ was obtained by treating LAlCl$_2$ with ammonia in the presence of an N-heterocyclic carbene.[5] In the current case, however, the preparation of the N*i*Pr$_2$- or N(SiMe$_3$)$_2$-substituted derivatives using LAlCl$_2$ as a precursor was not successful probably because of steric hindrance of the substituents. Aluminum has a relatively small atomic radius, and it is more easily shielded by the bulky β-diketiminato ligand when compared with ytterbium and samarium.[11,12] The procedure for the preparation of compounds **2** and **3** is an example for a successful introduction of a further bulky group on aluminum by changing the sequence of adding the components to the reaction mixture. A similar method was also found for the preparation of alkaline-earth metal derivatives.[15]

Synthesis of Bromide and Iodide Derivatives 5 and 6. The dibromide precursor LAlBr$_2$ (**4**) was readily prepared from LLi·OEt$_2$ with AlBr$_3$ in toluene. The ^{1}H NMR spectrum of **4** gives a pattern comparable to that of LAlCl$_2$ with one isopropyl methine septet and two methyl doublets of the β-diketiminato ligand,[19] demonstrating that the C_{2v} symmetry is kept in solution. The ^{27}Al NMR spectrum shows a resonance at δ 99.25 ppm, which is in the typical range for four-coordinate aluminum compounds.[20] The melting point of **4** (215 °C) is very close to that of its dichloride analogue (211–213 °C).[19] In the mass spectrum, the molecular ion is observed as the base peak, consistent with the observation for a related organoaluminum dibromide HC[C(Me)N(C$_6$F$_5$)]$_2$AlBr$_2$.[21]

The synthesis of LAl(Br)NMe$_2$ (**5**) parallels that used for the preparation of **1**, from the reaction of **4** with 1 equiv of LiNMe$_2$ to afford a light-pink solid in moderate yield. However, the analogous reactions aiming at LAl(Br)N*i*Pr$_2$ and LAl(Br)N(SiMe$_3$)$_2$ gave the target product containing always an equivalent amount of **4** as determined by ^{1}H NMR spectroscopy. All attempts to isolate the pure compounds

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(16) (a) Bradley, D. C. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 259. (b) Rutherford, D.; Atwood, D. A. *Organometallics* **1996**, *15*, 4417–4422. (c) Passarelli, V.; Carta, G.; Rossetto, G.; Zanella, P. *Dalton Trans.* **2003**, 1284–1291.

(17) Heine, A.; Stalke, D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 854–855.

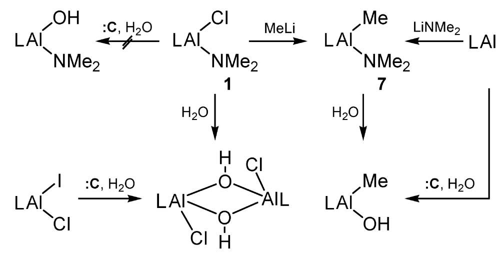
(18) Montero, M. L.; Wessel, H.; Roesky, H. W.; Teichert, M.; Usón, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 629–631.

(19) Stender, M.; Eichler, B. E.; Hardman, N. J.; Power, P. P.; Prust, J.; Noltemeyer, M.; Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 2794–2799.

(20) Cui, C.; Köpke, S.; Herbst-Irmer, R.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Wrackmeyer, B. *J. Am. Chem. Soc.* **2001**, *123*, 9091–9098.

(21) Yang, Z.; Zhu, H.; Ma, X.; Chai, J.; Roesky, H. W.; He, C.; Magull, J.; Schmidt, H.-G.; Noltemeyer, M. *Inorg. Chem.* **2006**, *45*, 1823–1827.

Scheme 2



by repeated recrystallization from various organic solvents were not successful. Possibly an equilibrium exists in these systems, which could not be driven further by the elimination of alkali bromide.

Treatment of $LAlI_2$ with 1 equiv of $LiNMe_2$ in toluene smoothly afforded $LAl(I)NMe_2$ (**6**). A reference reaction of LAl(I)Cl with a stoichiometric amount of $LiNMe_2$ selectively gave the expected **1** under elimination of lithium iodide, due to the weaker Al−I bond strength. Similarly, in a recent example of the stepwise hydrolysis of LAl(I)Cl, the iodide is more easily removed than chloride by the elimination of $[H:\mathbf{C}]^+I^-$ as a precipitate.[22] The ^1H NMR spectra of **5** and **6** show a pattern similar to that of **1**, confirming the analogous composition.

Alkylation of Compounds 1–3. Treatment of compounds **1** and **2** with MeLi, respectively, resulted in the formation of the corresponding methylated compounds $LAl(Me)NR_2$ (**7**, R = Me; **8**, R = *i*Pr). An alternative route allowed access to compound **7** from the reaction of LAl(Me)Cl with $LiNMe_2$ in toluene in modest yield. In contrast, no reaction of **3** could be observed with the bulky $N(SiMe_3)_2$ group.

The ^1H NMR spectrum of **7** exhibits a singlet at high field (δ −0.87 ppm), demonstrating the presence of a methyl group at the Al atom. The proton resonance of NMe_2 is again observed as a singlet (δ 2.68 ppm). In the mass spectrum, the base peak is assigned to the fragment $[M^+ - Me - NMe_2]$. The methyl proton resonance of **8** (δ −0.09 ppm) is shifted downfield relative to those found in **7** and LAl(Me)Cl (δ −0.64 ppm).[22] The highest peak in the mass spectrum of **8** corresponds to the fragment $[M^+ - NiPr_2]$.

Fluorination of Compounds 1–3. The reaction of **1**−**3** with 1 equiv of Me_3SnF in toluene under reflux overnight readily produced $LAl(F)NR_2$ (**9**, R = Me; **10**, R = *i*Pr; **11**, R = $SiMe_3$) in high yield. Again, it is demonstrated that Me_3SnF can be used in stoichiometric amounts rather than in an excess for metathesis reactions.[23]

The ^1H NMR spectra of **9** and **10** are very similar to those of the respective chloride analogues. In the ^1H NMR spectrum of **11**, it is interesting to note that one of the $N(SiMe_3)_2$ proton resonances (δ 0.15 ppm) is split into a doublet with a long-range coupling constant of $^5J_{F-H}$ = 1.8 Hz. In the mass spectra of **9**−**11**, the most intense peak is assigned to the fragment $[M^+ - Me]$.

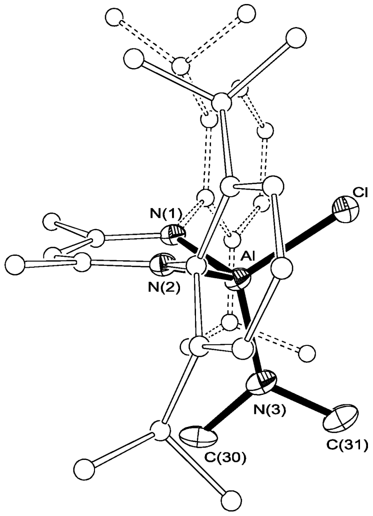


Figure 1. Molecular structure of **1**. All H atoms are omitted for clarity.

Hydrolysis of Compounds 1 and 7. Controlled hydrolysis of compound **1** in the presence of an N-heterocyclic carbene[5,22,24] resulted in the free ligand LH rather than the desired aluminum hydroxide $LAl(OH)NMe_2$ (Scheme 2). Probably under these conditions, the coexistence of both a hydroxyl group and an amido group on the Al atom [as an intermediate $LAl(OH)NMe_2$] may be unstable and prone to decomposition by intramolecular elimination of LH. In contrast, direct hydrolysis of **1** and **7** by 1 equiv of distilled water in toluene at 0 °C led to the isolation of the known compounds $[LAlCl(\mu\text{-}OH)]_2$[22] and LAl(Me)OH,[25] respectively, in low yield. The latter compounds had before been accessed by controlled hydrolysis under elimination of hydrogen halide,[22,25] as shown in Scheme 2.

Structural Characterization of 1−3. Molecular structures of **1**−**3** were determined by X-ray diffraction. Single crystals of **1** and **3** were recovered from a concentrated toluene solution at room temperature, while those of **2** were grown from a THF solution. The structures of compounds **1**−**3** are shown in Figures 1−3, with selected bond lengths and angles provided in Table 1. Details for crystal data and structure refinement are listed in Table 2.

Compounds **1**−**3** each adopt a monomeric structure in which the Al atom is coordinated to one Cl atom and three N atoms (one from the amido group and the other two from the β-diketiminato ligand).

1 crystallizes in the triclinic space group $P\bar{1}$. The six-membered C_3N_2Al ring is slightly folded in a typical envelope conformation,[11] where the C atoms are displaced by 34° from the N(1)−Al−N(2) plane. The Cl atom and the amido group are located on opposite sides of the six-membered C_3N_2Al ring. The Al−Cl bond length [2.1339(7) Å] is comparable to that of $LAlCl_2$ [2.1344(4) and 2.1185(4) Å].[19] The Al−N(3) bond length [1.7882(15) Å] is near the

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[22] Zhu, H.; Chai, J.; He, C.; Bai, G.; Roesky, H. W.; Jancik, V.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **2005**, *24*, 380–384.

[23] (a) Herzog, A.; Liu, F.-Q.; Roesky, H. W.; Demsar, A.; Keller, K.; Noltemeyer, M.; Pauer, F. *Organometallics* **1994**, *13*, 1251–1256. (b) Guzyr, O. I.; Schormann, M.; Schimkowiak, J.; Roesky, H. W.; Lehmann, C.; Walawalkar, M. G.; Murugavel, R.; Schmidt, H.-G.; Noltemeyer, M. *Organometallics* **1999**, *18*, 832–836.

[24] (a) Pineda, L. W.; Jancik, V.; Roesky, H. W.; Neculai, D.; Neculai, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 1419–1421. (b) Singh, S.; Jancik, V.; Roesky, H. W.; Herbst-Irmer, R. *Inorg. Chem.* **2006**, *45*, 949–951.

[25] Bai, G.; Singh, S.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G. *J. Am. Chem. Soc.* **2005**, *127*, 3449–3455.

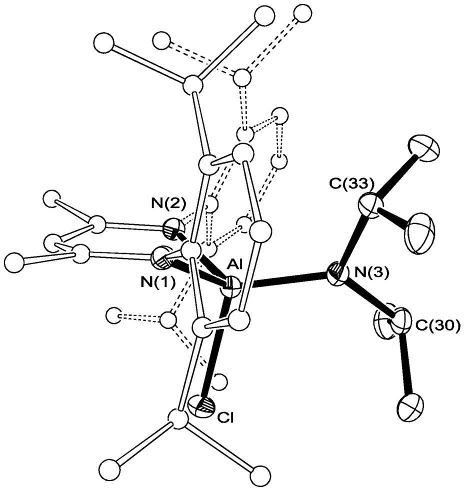

Figure 2. Molecular structure of **2**. All H atoms are omitted for clarity.

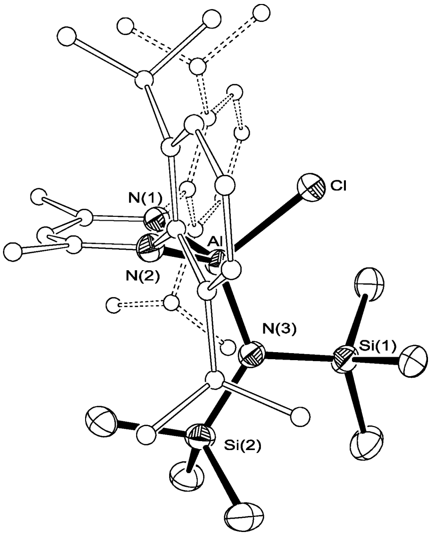

Figure 3. Molecular structure of **3**. All H atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of **1**−**3**

	1[a]	**2**[b]	**3**[c]
Al−N(1)	1.8912(14)	1.8992(11)	1.9178(12)
Al−N(2)	1.9054(14)	1.9291(11)	1.9031(12)
Al−N(3)	1.7882(15)	1.7996(11)	1.8361(12)
Al−Cl	2.1339(7)	2.1576(5)	2.1532(5)
N(2)−Al−N(1)	96.15(6)	96.56(5)	98.07(5)
N(3)−Al−Cl	110.59(5)	112.21(4)	110.92(4)
C′−N(3)−C″	113.00(14)	113.19(10)	118.36(7)
C′−N(3)−Al	119.48(12)	119.89(9)	116.20(6)
C″−N(3)−Al	127.18(12)	126.89(9)	125.25(7)

[a] C′ = C(30); C″ = C(31). [b] C′ = C(33); C″ = C(30). [c] C′ = Si(1); C″ = Si(2).

lower end of the predicted range of 1.79−1.85 Å[26] and close to those in [$Me_2NC(N\textit{i}Pr)_2$]$Al(NMe_2)_2$ [1.788(3) and 1.797(3) Å].[6] However, in some related examples for Al-bound terminal NMe_2 groups, the Al−N distances are found to be variable with the steric crowding, ranging from 1.775(4) Å in [$AlCl(MeNCH_2CH_2NMe)_2(Al(NMe_2)Cl)(Al(NMe_2)_2)$][27] to 1.802 Å (av) in [$Al(NMe_2)_3$]$_2$[4] and even 1.822(2) Å in [$Me_2NC(N\textit{i}Pr)_2$]$_2AlNMe_2$.[6]

Table 2. Crystal Data and Structure Refinement of **1**−**3**

	1	**2**	**3**
CCDC	659515	659516	660534
formula	$C_{31}H_{47}AlClN_3$	$C_{35}H_{55}AlClN_3$	$C_{35}H_{59}AlClN_3Si_2$
fw	524.15	580.25	640.46
temp, K	100(2)	100(2)	133(2)
cryst syst	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/n$	$Pbcn$
a, Å	10.5043(8)	10.0276(8)	20.3830(5)
b, Å	12.3521(10)	20.3125(16)	18.1958(4)
c, Å	13.4442(11)	16.7958(13)	20.0821(5)
α, deg	66.4120(10)	90	90
β, deg	72.1260(10)	97.4050(10)	90
γ, deg	72.6120(10)	90	90
V, Å^3	1490.2(2)	3392.5(5)	7448.1(3)
Z	4	4	8
ρ_c, Mg/m^3	1.168	1.136	1.142
μ, mm^{-1}	0.181	0.165	0.218
$F(000)$	568	1264	2784
θ range, deg	1.69−26.41	2.64−25.21	1.50−24.84
index ranges	$-12 \le h \le 13$ $-13 \le k \le 15$ $0 \le l \le 16$	$-12 \le h \le 11$ $0 \le k \le 24$ $0 \le l \le 20$	$-23 \le h \le 24$ $-21 \le k \le 21$ $-23 \le l \le 23$
reflns collected	27 557	38 060	72 208
indep reflns (R_{int})	6084 (0.0309)	6089 (0.0264)	6420 (0.0394)
data/restraints/param	6084/0/337	6089/0/375	6420/0/395
GOF on F^2	1.034	1.039	1.065
R1, wR2 [$I > 2\sigma(I)$]	0.0394, 0.1026	0.0329, 0.0877	0.0294, 0.0823
R1, wR2 (all data)	0.0502, 0.1098	0.0379, 0.0918	0.0341, 0.0845
largest diff peak/ hole, e/Å^3	0.503/−0.289	0.286 /−0.282	0.218/−0.253

2 crystallizes in the monoclinic space group $P2(1)/n$. The same envelope conformation as that found in **1** is also recognized in this structure, with a folding angle of 43°. Compared to **1**, however, the positions of the Cl atom and the amido group are exchanged. The Al−Cl bond length [2.1576(5) Å] is consistent with those reported for LAl(Me)Cl [2.158(1) Å][28] and LAl(I)Cl [2.151(1) Å][22] but a little longer than that of **1** [2.1339(7) Å]. The Al−N(3) distance [1.7996(11) Å] agrees well with the average value of 1.795(5) Å in $Al(N\textit{i}Pr_2)_3$.[26]

3 crystallizes in the orthorhombic space group *Pbcn*. Compounds **3** and **1** are structurally similar concerning the arrangement of the Cl atom and the amido group relative to the six-membered C_3N_2Al ring. The folding angle (33°) is also close to that of **1** (34°). The Al−Cl bond length [2.1532(5) Å] is slightly shorter but comparable to that of **2** [2.1576(5) Å]. The Al−N(3) separation [1.8361(12) Å] is very close to those of [$((Me_3Si)_2N)_2Al(\mu\text{-}CH_2)$]$_2$ [1.832(3) and 1.837(3) Å][29] while longer than those of $Mes_2AlN(SiMe_3)_2$ [1.813(7) Å][8] and of the dimeric iminoalane [1.790 and 1.818. Å] containing three-coordinate Al centers[30] and shorter than that of [$(Me_3Si)_2N$]$_2AlH_2Li\cdot 2Et_2O$ (av 1.862 Å) with the four-coordinate Al center.[17]

The Al−N(1) and Al−N(2) bond lengths (1.891–1.929 Å) in **1**−**3** are close to the ones reported[9,22,28,31] and obviously longer than the Al−N(3) distances (1.788–1.836

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(26) Brothers, P. J.; Wehmschulte, R. J.; Olmstead, M. M.; Ruhlandt-Senge, K.; Parkin, S. R.; Power, P. P. *Organometallics* **1994**, *13*, 2792–2799.

(27) Leggett, G.; Motevalli, M.; Sullivan, A. C. *J. Organomet. Chem.* **2000**, *598*, 36–41.

(28) Singh, S.; Ahn, H. J.; Stasch, A.; Jancik, V.; Roesky, H. W.; Pal, A.; Biadene, M.; Herbst-Irmer, R.; Noltemeyer, M.; Schmidt, H.-G. *Inorg. Chem.* **2006**, *45*, 1853–1860.

(29) Knabel, K.; Nöth, H.; Seifert, T. *Z. Naturforsch. B* **2002**, *57*, 830–833.

(30) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 969–970.

(31) Qian, B.; Ward, D. L.; Smith, M. R., III. *Organometallics* **1998**, *17*, 3070–3076.

Å), resulting from the electronically delocalized *β*-diketiminato ligand. Furthermore, the Al−N(3) bond lengths in **1**−**3** increase with the steric demand of the amido substituents, which is in accordance with the trend in a previous theoretical study of the electronic structure of $Al(NR_2)_3$ (R = H, Me, *i*Pr, $SiMe_3$).[32] In each case of **1**−**3**, the N(3) atom favors a nearly trigonal coordination geometry because the sum of the angle at the nitrogen of the amido groups is very close to 360° (**1**, 359.66°; **2**, 359.97°; **3**, 359.81°). The NC_2 plane in **1** is almost perpendicular to the quasi-NCCN plane (89.73°), while the NC_2 plane in **2** and the NSi_2 plane in **3** are tilted to some degree as a result of diminishing steric repulsion (**2**, 63.83°; **3**, 87.33°).[26,32]

NMR Characterization of 1–11. As was previously noted for the mixed halide LAl(I)Cl,[22] an asymmetric substitution of the Al atom with one halogen and one amido group in $LAl(X)NR_2$ results in two nonequivalent sides of the six-membered C_3N_2Al ring of the *β*-diketiminato ligand. Subsequently, each subspectrum of the ligand contains two isopropyl groups (evident as two isopropyl methine septets and four distinct methyl doublets) and three distinct aromatic CH groups, representing both symmetry-related Ar substituents.

Using NOESY (nuclear Overhauser enhancement) spectra, all ^1H NMR resonances can be stereospecifically assigned to individual atoms in the 3D structure. For example, in **1** only one methyl group of the *β*-diketiminato ligand shows a NOE correlation with the NMe_2 group, while two show NOE correlations with the protons of the *β*-diketiminato core on the reverse side of the Ar ring. No N−Ar bond rotation was observed. The corresponding ^{13}C NMR resonances were identified from 2D $^1H-^{13}C$ correlation spectra optimized for single and multiple bond correlations.

1 and **9** exhibit single ^1H and ^{13}C NMR resonances for the NMe_2 group, indicating that the rotation about the Al−N(3) bond is fast in solution. For **5**, however, we noticed a substantial broadening of the ^1H NMR resonance for the NMe_2 group at 500 vs 200 MHz, concomitant with a broadening of the ^{13}C NMR resonance at 125 MHz. It is suggested that in this compound the Al−N(3) bond rotation is somewhat slowed down because of a steric effect of the larger Br atom and thus approaches the chemical shift time scale. This observation could be confirmed by further broadening (by a factor of 2.7) of the ^1H and ^{13}C NMR resonances for the NMe_2 group when the temperature was lowered to 10 °C. In the case of **6**, we observed a very broad ^1H NMR resonance at ambient temperature at 200 MHz, which splits into two broad resonances (*δ* 2.79 and 2.64 ppm) at 500 MHz. Here, lowering the temperature (10 °C) resulted in approximately a 2.7-fold narrowing of both resonances. From the line width, we calculated that the rate of Al−N(3) bond rotation for **6** is in the order of 120 s^{-1} at 25 °C and 45 s^{-1} at 10 °C, but in its bromide analogue **5**, it is at least 20 times faster. In the series of the dimethylamides LAl(X)-NMe_2 (**9**, X = F; **1**, X = Cl; **5**, X = Br; **6**, X = I), the amido ^1H NMR resonance is shifted increasingly upfield (*δ* 2.48 to av 2.72 ppm) with increasing electronegativity of the halogen.

Surprisingly, **2** and **10** exhibit a single septet and a single doublet for the methine and methyl protons of the N*i*Pr_2 group and also single resonances in the ^{13}C NMR spectra under all conditions studied. With regard to the steric demand of an isopropyl group, the Al−N(3) bond would be expected to rotate rather slowly. Possibly, as seen in the structure of **2** (Figure 2), the N*i*Pr_2 group stretches itself out away from the clasp of the Ar flanks and adopts a pseudoequatorial position with respect to the six-membered C_3N_2Al ring, thereby gaining more space for a flexible Al−N(3) bond rotation.

Further increasing the steric demand of the amido group in **3** and **11** gave separate ^1H, ^{13}C, and ^{29}Si NMR resonances for the two $SiMe_3$ substituents, owing to the restricted rotation of the bulky $N(SiMe_3)_2$ group along the Al−N(3) linkage. Nevertheless, a plane of symmetry through the Al−X and Al−N(3) bonds is conserved in the NMR spectra, in agreement with the crystal structure of **3**, which shows the N(3) atom in a nearly sp^2-hybridized state. No exchange peaks between the two proton resonances for $SiMe_3$ substituents were observed in the NOESY spectra even at elevated temperature (60 °C), indicating that the rate of Al−N(3) bond rotation is extremely slow ($<0.01\ s^{-1}$). The NOESY spectrum of **11** also revealed that the $SiMe_3$ group that shows a split ^1H NMR resonance ($^5J_{H-F} = 1.8$ Hz) is the one cis to the F atom. A similar behavior was observed for the corresponding ^{13}C NMR resonance ($^4J_{C-F} = 4.3$ Hz), whereas both ^{29}Si NMR resonances are doublets ($^3J_{Si-F} = 3.4$ and 3.2 Hz). Possibly, the spatial proximity of the *cis*-$SiMe_3$ group and the F atom favors a "through-space" coupling due to the $^5J_{H-F}$, $^4J_{C-F}$ and, $^3J_{Si-F}$ (partly) couplings.

Conclusion

Monomeric aluminum halide amides with the general formula $LAl(X)NR_2$ were prepared. Treatment of $LAlX_2$ with $LiNMe_2$ gives the compounds **1**, **5**, and **6**, respectively. When more bulky substituents were employed, **2** and **3** are accessible by the one-pot reaction of $AlCl_3$, LiN*i*Pr_2 or $KN(SiMe_3)_2$ and $LLi \cdot OEt_2$. The methylated compounds **7** and **8** were prepared by the reaction of MeLi with **1** and **2**. Using Me_3SnF as a fluorinating agent, **1**−**3** were converted by metathesis to **9**−**11**. The hydrolysis of **1** and **7** resulted in the known aluminum hydroxides $[LAlCl(\mu\text{-}OH)]_2$ and LA(Me)OH, while the protocol of hydrolyzing Al−Cl of **1** led to decomposition. Presently, the reduction of $LAl(X)NR_2$ as a precursor to generate either a stable radical or a compound with an Al−Al bond is in progress.

Experimental Section

General Remarks. All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. The samples for reactions as well as for analytical measurements were manipulated in a glovebox. Solvents were purified and dried using conventional procedures and were freshly distilled under nitrogen and degassed prior to use. $AlCl_3$, $AlBr_3$,

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[32] Fleurat-Lessard, P.; Volatron, F. *Inorg. Chem.* **2000**, *39*, 1849–1854.

LiNMe$_2$, LiN*i*Pr$_2$, LiN(SiMe$_3$)$_2$, NaN(SiMe$_3$)$_2$, KN(SiMe$_3$)$_2$, and MeLi were purchased from Aldrich. LH,[31,33] LLi·OEt$_2$,[31,33] LAlCl$_2$,[19] LAl(Me)Cl,[25] LAl(I)Cl,[22] LAlMe$_2$,[31] LAlI$_2$,[34] Me$_3$SnF,[35] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (abbreviated as **:C**)[36] were prepared as described in the literature.

LAl(Cl)NMe$_2$ (1). A solution of LiNMe$_2$ (0.11 g, 2 mmol) in toluene (30 mL) was added at −78 °C to a solution of LAlCl$_2$ (1.03 g, 2 mmol) in toluene (30 mL). The mixture was allowed to warm to room temperature and stirred overnight. Volatile components were removed in vacuo, and the crude product was extracted with Et$_2$O (60 mL). The extract was evaporated to dryness to afford **1** as a white solid. Single crystals of X-ray-quality were grown from the concentrated toluene solution at room temperature. Yield: 0.81 g (77%). Mp: 186–187 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 1.08 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.21 (d, $J = 7.0$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.33 (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.45 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.52 (s, 6 H, C*Me*), 2.64 (s, 6 H, N(C*H*$_3$)$_2$), 3.30 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 3.53 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 4.87 (s, 1 H, γ-C*H*), 7.10–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 170.9 (*C*N), 145.0, 144.4, 140.1, 127.7, 124.9, 124.6 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 97.9 (γ-*C*H), 40.8 (N(*C*H$_3$)$_2$), 29.0, 28.3 (*C*H(CH$_3$)$_2$), 25.5, 24.8, 24.7, 24.6 (CH(*C*H$_3$)$_2$), 23.5 (β-*C*H$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1589 (w), 1527 (m), 1318 (m), 1261 (m), 1162 (w), 1101 (w), 1057 (w), 1019 (w), 981 (w), 937 (w), 877 (w), 834 (w), 801 (m), 759 (w), 722 (w), 649 (w), 634 (w). EI-MS: m/z (%) 523.4 (8) [M$^+$], 508.3 (40) [M$^+$ − Me], 479.3 (8) [M$^+$ − NMe$_2$], 463.3 (100) [M$^+$ − Me − NMe$_2$]. Anal. Calcd for C$_{31}$H$_{47}$AlClN$_3$ (524.20): C, 71.03; H, 9.04; N, 8.02. Found: C, 70.67; H, 8.90; N 7.90.

LAl(Cl)N*i*Pr$_2$ (2). A solution of LiN*i*Pr$_2$ (0.55 g, 5 mmol) in toluene (30 mL) was added at −78 °C to the suspension of freshly sublimed AlCl$_3$ (0.67 g, 5 mmol) in toluene (30 mL). The mixture was allowed to warm to room temperature, and a white precipitate was observed. After this mixture was stirred overnight, a solution of LLi·OEt$_2$ (2.49 g, 5 mmol) in toluene (20 mL) was added at −78 °C. Then the cold bath was removed to allow the mixture to warm to room temperature under stirring for another 12 h. After filtration, the filtrate was evaporated to dryness to afford **2** as a white solid. Single crystals of X-ray-quality were grown from THF solution. Yield: 0.78 g (27%). Mp: 263 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 0.84 (d, $J = 6.7$ Hz, 12 H, N(CH(C*H*$_3$)$_2$)$_2$), 0.98 (d, $J = 6.7$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.17 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.29 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.56 (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.60 (s, 6 H, C*Me*), 3.10 (sept, $J = 6.8$ Hz, 2 H, N(C*H*(CH$_3$)$_2$)$_2$), 3.16 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 3.89 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 5.11 (s, 1 H, γ-C*H*), 7.05–7.20 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 171.6 (*C*N), 146.1, 142.7, 141.9, 127.4, 125.5, 123.9 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 99.9 (γ-*C*H), 46.9 (N(*C*H(CH$_3$)$_2$)$_2$), 29.4, 28.2 (*C*H(CH$_3$)$_2$), 26.4 (N(CH(*C*H$_3$)$_2$)$_2$), 25.7, 25.1, 24.8 (CH(*C*H$_3$)$_2$), 24.5 (β-*C*H$_3$), 23.8 (CH(*C*H$_3$)$_2$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3059 (s), 2727 (s), 1938 (w), 1870 (w), 1590 (w), 1549 (s), 1533 (s), 1518 (s), 1313 (s), 1297 (s), 1251 (s), 1193 (s), 1173 (s), 1156 (s), 1124 (m), 1098 (m), 1056 (m), 1018 (s), 1008 (s), 972 (s), 936 (m), 885 (m), 877 (m), 832 (w), 802 (m), 794 (m), 770 (m), 759 (m), 724 (m), 711 (w), 645 (m), 631 (m), 593 (m), 560 (s). EI-MS: m/z (%) 579 (4) [M$^+$], 564 (40) [M$^+$ − Me], 479 (100) [M$^+$ − N*i*Pr$_2$]. Anal. Calcd for C$_{35}$H$_{55}$AlClN$_3$ (580.30): C, 72.45; H, 9.55; N, 7.24. Found: C, 72.35; H, 9.52; N, 7.22.

LAl(Cl)N(SiMe$_3$)$_2$ (3). A solution of KN(SiMe$_3$)$_2$ (1.05 g, 5 mmol) in toluene (30 mL) was added to the suspension of freshly sublimed AlCl$_3$ (0.67 g, 5 mmol) in toluene (30 mL) at −78 °C. The mixture was stirred for 4 h at room temperature, and a solution of LLi·OEt$_2$ (2.49 g, 5 mmol) in toluene (20 mL) was added at −78 °C. The mixture was allowed to warm to room temperature and stirred overnight. After filtration, the filtrate was evaporated and washed with cold *n*-hexane (5 mL) to afford LAl(Cl)N(SiMe$_3$)$_2$ as a white solid. Single crystals of X-ray-quality were grown from toluene solution. Yield: 1.48 g (46%). Mp: 173–175 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 0.30 (s, 9 H, Si(C*H*$_3$)$_3$), 0.42 (s, 9 H, Si(C*H*$_3$)$_3$), 1.08 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.19 (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.39 (d, $J = 6.6$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.44 (s, 6 H, C*Me*), 1.45 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 3.24 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 3.69 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 5.02 (s, 1 H, γ-C*H*), 7.10–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 172.5 (*C*N), 145.3, 144.5, 141.6, 127.8, 125.4, 124.8 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 102.2 (γ-*C*H), 28.8, 28.2 (*C*H(CH$_3$)$_2$), 25.8, 25.4, 25.4 (CH(*C*H$_3$)$_2$), 25.1 (β-*C*H$_3$), 24.9 (CH(*C*H$_3$)$_2$), 7.13, 6.00 (Si(*C*H$_3$)$_3$) ppm. ^{29}Si NMR (99.36 MHz, C$_6$D$_6$): δ 2.24, −3.20 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3064 (m), 1519 (m), 1318 (m), 1259 (m), 1246 (m), 1168 (w), 1109 (w), 1056 (w), 1019 (w), 937 (w), 907 (m), 877 (m), 837 (m), 798 (m), 773 (w), 758 (w), 724 (w), 668 (w), 649 (w), 607 (w), 554 (w), 538 (w), 485 (w), 451 (w), 396 (w). EI-MS: m/z (%) 639.4 (4) [M$^+$], 624.4 (100) [M$^+$ − Me]. Anal. Calcd for C$_{35}$H$_{59}$AlClN$_3$Si$_2$ (640.50): C, 65.64; H, 9.29; N, 6.56. Found: C, 65.59; H, 9.16; N, 6.51.

LAlBr$_2$ (4). A toluene solution (40 mL) of LLi·OEt$_2$ (1.50 g, 3 mmol) was added drop by drop to a suspension of freshly sublimed AlBr$_3$ (0.80 g, 3 mmol) at −32 °C with rapid stirring. The mixture was allowed to warm to room temperature overnight. After filtration, the concentrated solution was kept at −4 °C overnight to afford colorless crystals. Yield: 1.12 g (62%). Mp: 215 °C. ^{1}H NMR (C$_6$D$_6$, 300.13 MHz): δ 1.08 (d, 12 H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 1.42 (d, 12 H, $J = 6.8$ Hz, CH(C*H*$_3$)$_2$), 1.50 (s, 6 H, C*Me*), 3.49 (sept, 4 H, $J = 6.8$ Hz, C*H*(CH$_3$)$_2$), 4.96 (s, 1 H, γ-CH), 7.09–7.15 (m, *Ar*) ppm. ^{13}C NMR (75.48 MHz, C$_6$D$_6$): δ 172.4 (*C*N), 144.8, 144.8, 138.5, 127.7, 125.0, 125.0 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 99.6 (γ-*C*H), 28.9 (*C*H(CH$_3$)$_2$), 25.9, 24.6 (CH(*C*H$_3$)$_2$), 23.8 (β-*C*H$_3$) ppm. ^{27}Al NMR (78.21 MHz, C$_6$D$_6$): δ 99.25 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 1590 (w), 1537 (m), 1515 (m), 1315 (s), 1297 (m), 1250 (m), 1189 (w), 1171 (m), 1106 (w), 1055 (w), 1021 (m), 936 (w), 891 (w), 799 (m), 788 (m), 758 (m), 722 (m), 645 (w). EI-MS: m/z (%) 604.1 (100) [M$^+$], 589.1 (20) [M$^+$ − Me]. Anal. Calcd for C$_{29}$H$_{41}$AlBr$_2$N$_2$ (604.4): C, 57.63; H, 6.84; N, 4.63. Found: C, 57.27; H, 7.00; N, 4.52.

LAl(Br)NMe$_2$ (5). The preparation of **5** was accomplished like that of **1** from **4** (1.81 g, 3 mmol) and LiNMe$_2$ (0.16 g, 3 mmol) to afford a light-pink solid. Yield: 0.78 g (46%). Mp: 202–203 °C. ^{1}H NMR (500.13 MHz, C$_6$D$_6$): δ 1.07 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.21 (d, $J = 7.0$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.31 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.45 (d, $J = 6.8$ Hz, 6 H, CH(C*H*$_3$)$_2$), 1.51 (s, 6 H, C*Me*), 2.67 (br, 6 H, N(C*H*$_3$)$_2$), 3.31 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 3.33 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH$_3$)$_2$), 4.88 (s, 1 H, γ-C*H*), 7.10–7.17 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C$_6$D$_6$): δ 170.9 (*C*N), 145.0, 144.2, 140.2, 127.7, 124.6, 124.5 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 98.3 (γ-*C*H), 41.1 (br, N(*C*H$_3$)$_2$), 29.1, 28.3 (*C*H(CH$_3$)$_2$), 25.6, 24.8, 24.7, 24.7 (CH(*C*H$_3$)$_2$), 23.7 (β-*C*H$_3$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2785 (s), 2768 (s), 1660 (m), 1591 (m), 1546 (m), 1527 (m), 1317 (m), 1261 (m), 1174 (m), 1160 (m), 1099 (m), 1019 (m), 981 (m), 937 (w), 876 (w), 834 (w), 800 (m),

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(33) Budzelaar, P. H. M.; van Oort, A. B.; Orpen, A. G. *Eur. J. Inorg. Chem.* **1998**, 1485–1494.

(34) Cui, C.; Roesky, H. W.; Schmidt, H.-G.; Noltemeyer, M.; Hao, H.; Cimpoesu, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 4274–4276.

(35) Krause, E. *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 1447–1456.

(36) Kuhn, N.; Kratz, T. *Synthesis* **1993**, 561–562.

768 (w), 722 (w), 648 (w). EI-MS: *m*/*z* (%) 569.3 (10) $[\mathrm{M^+}]$, 552.3 (40) $[\mathrm{M^+ - Me}]$, 523.2 (20) $[\mathrm{M^+ - NMe_2}]$, 507.3 (100) $[\mathrm{M^+ - Me - NMe_2}]$. Anal. Calcd for $\mathrm{C_{31}H_{47}AlBrN_3}$ (568.60): C, 65.48; H, 8.33; N, 7.39. Found: C, 64.88; H, 8.33; N, 7.23.

$\mathbf{LAl(I)NMe_2}$ (6). The preparation of **6** was accomplished like that of **1** from $\mathrm{LAlI_2}$ (1.39 g, 2 mmol) and $\mathrm{LiNMe_2}$ (0.11 g, 2 mmol). Yield: 0.85 g (69%). Mp: 192–195 °C. ^{1}H NMR (500.13 MHz, $\mathrm{C_6D_6}$): δ 1.05 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.21 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.35 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.46 (d, J = 7.0 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.52 (s, 6 H, C*Me*), 2.79 (br, 3 H, $\mathrm{N(C}H_3\mathrm{)_2}$), 2.64 (br, 3 H, $\mathrm{N(C}H_3\mathrm{)_2}$), 3.29 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.34 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.89 (s, 1 H, γ-C*H*), 7.00–7.16 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, $\mathrm{C_6D_6}$): δ 170.7 (*C*N), 145.2, 143.9, 140.5, 127.7, 124.7, 124.6 (*o*-, *o*-, *i*-, *p*-, *m*-, *m*-*Ar*), 98.6 (γ-*C*H), 40.2, 40.5 (br, $\mathrm{N(}C\mathrm{H_3)_2}$), 29.3, 29.2 ($C\mathrm{H(CH_3)_2}$), 25.7, 24.7, 24.7, 24.5 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 24.0 ($\beta$-$C\mathrm{H_3}$) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2786 (s), 2764 (s), 1589 (w), 1544 (m), 1524 (s), 1314 (s), 1253 (s), 1174 (m), 1156 (s), 1106 (m), 1067 (m), 1057 (m), 1017 (s), 978 (s), 936 (m), 875 (m), 798 (s), 758 (m), 727 (s), 694 (w), 646 (m), 631 (m), 551 (m). EI-MS: *m*/*z* (%) 615.3 (4) $[\mathrm{M^+}]$, 600.2 (12) $[\mathrm{M^+ - Me}]$, 571.2 (100) $[\mathrm{M^+ - NMe_2}]$. Anal. Calcd for $\mathrm{C_{31}H_{47}AlIN_3}$ (615.6): C, 60.48; H, 7.70; N, 6.83. Found: C, 60.32; H, 7.58; N, 6.58.

$\mathbf{LAl(Me)NMe_2}$ (7). Route a: At −78 °C, MeLi (1 mL, 1.6 M, 1.6 mmol) was added to a solution of **1** (0.84 g, 1.6 mmol) in toluene (40 mL). The mixture was allowed to warm to room temperature and stirred overnight. After filtration, the solution was concentrated to give a colorless crystalline solid. Yield: 0.48 g (59%). Route b: A solution of LAl(Me)Cl (0.99 g, 2 mmol) in toluene (30 mL) was added at −78 °C to the suspension of $\mathrm{LiNMe_2}$ (0.11 g, 2 mmol) in toluene (20 mL). The mixture was allowed to warm to room temperature and stirred overnight. After filtration, the solution was concentrated to give a colorless crystalline solid. Yield: 0.54 g (53%). Mp: 196–198 °C. ^{1}H NMR (500.13 MHz, $\mathrm{C_6D_6}$): δ −0.87 (s, 3 H, Al*Me*), 1.06 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.26 (d, J = 7.0 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.31 (d, J = 7.0 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.36 (d, J = 7.0 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.56 (s, 6 H, C*Me*), 2.68 (s, 6 H, $\mathrm{N(C}H_3\mathrm{)_2}$), 3.25 (sept, J = 7.0 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.47 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.90 (s, 1 H, γ-C*H*), 7.09–7.17 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, $\mathrm{C_6D_6}$): δ 169.1 (*C*N), 145.6, 143.64, 141.6, 127.1, 124.7, 124.1 (*o*-, *o*-, *i*-, *p*-, *m*-, *m*-*Ar*), 97.7 (γ-*C*H), 41.8 ($\mathrm{N(}C\mathrm{H_3)_2}$), 28.9, 28.1 ($C\mathrm{H(CH_3)_2}$), 25.9, 24.9, 24.7, 24.3 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 23.4 ($\beta$-$C\mathrm{H_3}$), −15.0 (br, Al*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 2759 (w), 2729 (w), 1934 (w), 1624 (w), 1546 (w), 1525 (w), 1316 (m), 1258 (w), 1192 (w), 1174 (w), 1162 (w), 1100 (w), 1065 (w), 1056 (w), 1017 (w), 978 (w), 936 (w), 870 (w), 797 (w), 761 (w), 723 (w), 680 (w), 650 (w). EI-MS: *m*/*z* (%) 503.4 (4) $[\mathrm{M^+}]$, 488.36 (16) $[\mathrm{M^+ - Me}]$, 459.3 (36) $[\mathrm{M^+ - NMe_2}]$, 443.3 (100) $[\mathrm{M^+ - Me - NMe_2}]$. Anal. Calcd for $\mathrm{C_{32}H_{50}AlN_3}$ (503.7): C, 76.30; H, 10.00; N, 8.34. Found: C, 75.91; H, 10.11; N, 8.17.

$\mathbf{LAl(Me)N}\boldsymbol{i}\mathbf{Pr_2}$ (8). At −78 °C, MeLi (0.94 mL, 1.6 M, 1.5 mmol) was added to a solution of **2** (0.58 g, 1 mmol) in toluene (40 mL). The mixture was allowed to warm to room temperature and stirred overnight. After filtration and removal of all of the volatiles, the residue was dissolved in toluene (10 mL) and kept at 4 °C overnight to afford a colorless crystalline solid. Yield: 0.35 g (62%). Mp: 245–247 °C. ^{1}H NMR (500.13 MHz, $\mathrm{C_6D_6}$): δ −0.09 (s, 3 H, Al*Me*), 0.82 (d, J = 6.4 Hz, 12 H, $\mathrm{N(CH(C}H_3\mathrm{)_2)_2}$), 1.06 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.16 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.35 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.48 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.58 (s, 6 H, C*Me*), 3.10 (sept, J = 6.8 Hz, 2 H, $\mathrm{N(C}H\mathrm{(CH_3)_2)_2}$), 3.30 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.47 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 5.00 (s, 1 H, γ-C*H*), 7.10–7.18 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, $\mathrm{C_6D_6}$): δ 170.6 (*C*N), 145.1, 143.3, 143.0, 126.8, 124.8, 124.1 (*o*-, *o*-, *i*-, *p*-, *m*-, *m*-*Ar*), 96.5 (γ-*C*H), 46.6 ($\mathrm{N(}C\mathrm{H(CH_3)_2)_2}$), 29.1, 28.0 ($C\mathrm{H(CH_3)_2}$), 26.8 ($\mathrm{N(CH(}C\mathrm{H_3)_2)_2}$), 25.2, 25.1, 25.0 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 24.5 ($\beta$-$C\mathrm{H_3}$), 23.1 ($\mathrm{CH(}C\mathrm{H_3)_2}$), −8.1 (br, Al*Me*) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3171 (w), 3058 (w), 1935 (w), 1867 (w), 1546 (w), 1524 (m), 1313 (m), 1251 (m), 1190 (w), 1172 (m), 1156 (w), 1107 (w), 1056 (w), 1011 (w), 964 (m), 937 (m), 868 (w), 833 (m), 793 (w), 765 (m), 744 (w), 724 (m), 680 (w), 642 (w), 603 (w). EI-MS: *m*/*z* (%) 544.42 (10) $[\mathrm{M^+ - Me}]$ 459.3 (100) $[\mathrm{M^+ - N}i\mathrm{Pr_2}]$. Anal. Calcd for $\mathrm{C_{36}H_{58}AlN_3}$ (559.8): C, 77.23; H, 10.44; N, 7.51. Found: C, 76.98; H, 10.05; N, 7.28.

$\mathbf{LAl(F)NMe_2}$ (9). Toluene (40 mL) was added to a mixture of **1** (0.84 g, 1.61 mmol) and $\mathrm{Me_3SnF}$ (0.30 g, 1.61 mmol). The mixture was then heated to reflux overnight until a clear solution was obtained. After filtration and removal of all of the volatiles, the residue was extracted with *n*-hexane (30 mL). The solution was concentrated and kept at 4 °C overnight to afford a colorless crystalline solid. Yield: 0.76 g (93%). Mp: 118–120 °C. ^{1}H NMR (500.13 MHz, $\mathrm{C_6D_6}$): δ 1.13 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.19 (d, J = 7.0 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.31 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.44 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.54 (s, 6 H, C*Me*), 2.48 (br, 6 H, $\mathrm{N(C}H_3\mathrm{)_2}$), 3.26 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.46 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 4.88 (s, 1 H, γ-C*H*), 7.05–7.20 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, $\mathrm{C_6D_6}$): δ 170.8 (*C*N), 144.8, 144.7, 140.0, 127.5, 124.7, 124.4 (*o*-, *o*-, *i*-, *p*-, *m*-, *m*-*Ar*), 97.4 (γ-*C*H), 40.4 ($\mathrm{N(}C\mathrm{H_3)_2}$), 28.6 (d, $^5J_{\mathrm{C-F}}$ = 1.9 Hz, $C\mathrm{H(CH_3)_2}$), 28.5 ($C\mathrm{H(CH_3)_2}$), 25.1 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 24.9 (d, $^6J_{\mathrm{C-F}}$ = 2.4 Hz, $\mathrm{CH(}C\mathrm{H_3)_2}$), 24.7, 24.6 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 23.2 ($\beta$-$C\mathrm{H_3}$) ppm. ^{19}F NMR (188.23 MHz, $\mathrm{C_6D_6}$): δ −15.03 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3121 (w), 3059 (w), 2778 (m), 1587 (w), 1535 (s), 1316 (m), 1276 (w), 1261 (m), 1195 (w), 1171 (m), 1101 (w), 1071 (w), 1057 (w), 1021 (m), 986 (m), 937 (w), 888 (w), 798 (m), 771 (m), 757 (w), 726 (w), 646 (w), 633 (w). EI-MS: *m*/*z* (%) 507.3 (20) $[\mathrm{M^+}]$, 492.3 (100) $[\mathrm{M^+ - Me}]$. Anal. Calcd for $\mathrm{C_{31}H_{47}AlFN_3}$ (507.7): C, 73.34; H, 9.33; N, 8.28. Found: C, 73.06; H, 9.15; N, 8.02.

$\mathbf{LAl(F)N}\boldsymbol{i}\mathbf{Pr_2}$ (10). The preparation of **10** was accomplished like that of **9** from **2** (0.58 g, 1 mmol) and $\mathrm{Me_3SnF}$ (0.19 g, 1 mmol). Yield: 0.50 g (89%). Mp: 223–225 °C. ^{1}H NMR (500.13 MHz, $\mathrm{C_6D_6}$): δ 0.80 (d, J = 6.8 Hz, 12 H, $\mathrm{N(CH(C}H_3\mathrm{)_2)_2}$), 0.99 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.19 (d, J = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.37 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.54 (d, J = 6.6 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.59 (s, 6 H, C*Me*), 2.96 (sept, J = 6.6 Hz, 2 H, $\mathrm{N(C}H\mathrm{(CH_3)_2)_2}$), 3.18 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.69 (sept, J = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 5.01 (s, 1 H, γ-C*H*), 7.05–7.20 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, $\mathrm{C_6D_6}$): δ 171.2 (*C*N), 145.4, 142.7, 142.2, 127.3, 124.0, 123.9 (*o*-, *o*-, *i*-, *p*-, *m*-, *m*-*Ar*), 98.6 (γ-*C*H), 46.2 ($\mathrm{N(}C\mathrm{H(CH_3)_2)_2}$), 29.3 ($C\mathrm{H(CH_3)_2}$), 27.8 (d, $^5J_{\mathrm{C\text{-}F}}$ = 3.1 Hz, $C\mathrm{H(CH_3)_2}$), 25.8 (d, $^4J_{\mathrm{C-F}}$ = 0.8 Hz, $\mathrm{N(CH(}C\mathrm{H_3)_2)_2}$), 25.1 (d, $^6J_{\mathrm{C-F}}$ = 1.5 Hz, $\mathrm{CH(}C\mathrm{H_3)_2}$), 24.9 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 24.7 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 24.2 ($\beta$-$C\mathrm{H_3}$), 23.7 ($\mathrm{CH(}C\mathrm{H_3)_2}$) ppm. ^{19}F NMR (188.23 MHz, $\mathrm{C_6D_6}$): δ 6.95 ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3060 (m), 1939 (w), 1872 (w), 1667 (w), 1623 (w), 1590 (w), 1550 (w), 1531 (s), 1518 (s), 1340 (w), 1316 (m), 1297 (m), 1252 (m), 1192 (m), 1169 (s), 1126 (m), 1107 (m), 1098 (m), 1057 (m), 1018 (m), 968 (m), 937 (m), 886 (w), 878 (m), 830 (w), 795 (m), 767 (m), 755 (m), 712 (w), 644 (w), 628 (m). EI-MS: *m*/*z* (%) 563.4 (10) $[\mathrm{M^+}]$, 548.4 (100) $[\mathrm{M^+ - Me}]$. Anal. Calcd for $\mathrm{C_{35}H_{55}AlFN_3}$ (563.8): C, 74.56; H, 9.83; N, 7.45. Found: C, 74.22; H, 9.64; N, 7.61.

$\mathbf{LAl(F)N(SiMe_3)_2}$ (11). The preparation of **11** was accomplished like that of **9** from **3** (1.03 g, 1.61 mmol) and $\mathrm{Me_3SnF}$ (0.30 g, 1.61 mmol). Yield: 0.91 g (91%). Mp: 173–175 °C. ^{1}H NMR

(500.13 MHz, C_6D_6): δ 0.15 (d, $^5J_{F-H} = 1.8$ Hz, 9 H, Si(CH_3)$_3$), 0.42 (s, 9 H, Si(CH_3)$_3$), 1.10 (d, $J = 6.8$ Hz, 6 H, CH(CH_3)$_2$), 1.19 (d, $J = 6.8$ Hz, 6 H, CH(CH_3)$_2$), 1.37 (d, $J = 6.8$ Hz, 6 H, CH(CH_3)$_2$), 1.41 (s, 6 H, C*Me*), 1.45 (d, $J = 6.8$ Hz, 6 H, CH(CH_3)$_2$), 3.24 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH_3)$_2$), 3.68 (sept, $J = 6.8$ Hz, 2 H, C*H*(CH_3)$_2$), 4.98 (s, 1 H, γ-C*H*), 7.05–7.20 (m, *Ar*) ppm. ^{13}C NMR (125.76 MHz, C_6D_6): δ 171.9 (*C*N), 145.1, 144.0, 141.0, 127.3, 125.1, 124.4 (*o*-, *o*-, *i*-, *p*-, *m*-, *m-Ar*), 100.8 (γ-*C*H), 28.2, 27.9 (*C*H(CH_3)$_2$), 25.7 (d, $^6J_{C\text{-}F} = 2.3$ Hz, CH(CH_3)$_2$), 25.2, 24.8, 24.4 (CH(CH_3)$_2$), 24.1 (d, $^4J_{C-F} = 1.0$ Hz, β-CH_3), 5.7 (Si(CH_3)$_3$), 5.0 (d, $^4J_{C-F} = 4.3$ Hz, Si(CH_3)$_3$) ppm. ^{19}F NMR (188.23 MHz, C_6D_6): δ 8.62 ppm. ^{29}Si NMR (99.36 MHz, C_6D_6): δ 2.00 (d, $^3J_{Si-F} = 3.2$ Hz), −4.34 (d, $^3J_{Si-F} = 3.4$ Hz) ppm. IR (Nujol mull, cm^{-1}): $\tilde{\nu}$ 3063 (s), 1866 (m), 1698 (m), 1662 (m), 1587 (m), 1531 (s), 1314 (m), 1259 (s), 1169 (m), 1096 (m), 1060 (m), 1021 (m), 931 (s), 882 (s), 833 (w), 820 (m), 798 (s), 761 (m), 724 (w), 673 (w), 651 (w). EI-MS: *m*/*z* (%) 623.4 (4) [M$^+$], 608.4 (100) [M$^+$ − Me]. Anal. Calcd for $C_{35}H_{59}AlFN_3Si_2$ (624.0): C, 67.37; H, 9.53; N, 6.73. Found: C, 66.73; H, 9.35; N, 6.59.

X-ray Structure Determination of 1−3. The data for **1** were collected from shock-cooled crystals at 100(2) K on a Bruker SMART-APEX II diffractometer with a D8 goniometer,[37] for **2** at 100(2) K on a Bruker TXS-Mo rotating anode with an APEX II detector on a D8 goniometer, and for **3** at 133(2) K on a Stoe IPDS-2. All diffractometers were equipped with a low-temperature device. The Bruker SMART-APEX II diffractometer and the Stoe IPDS-2 used graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. The Bruker TXS-Mo rotating anode used INCOATEC Helios mirror optics as the radiation monochromator. The data of **1** and **2** were integrated with *SAINT*,[38] and an empirical absorption (*SADABS*) was applied.[39] The data collection and reduction of **3** were performed with *X-Area* and *X-RED32*.[40] The structures were solved by direct methods (*SHELXS-97*)[41] and refined by full-matrix least-squares methods against F^2 (*SHELXL-97*).[42] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 C atoms and 1.2 times for all other C atoms. Other structural details are listed in Table 2. Crystallographic data for the structures **1**−**3** have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers are listed in Table 2. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (int code) +44(1223)336-033; or e-mail deposit@ccdc.cam.ac.uk.

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Supporting Information Available: X-ray structural information in CIF format for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) (a) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615–619. (b) Stalke, D. *Chem. Soc. Rev.* **1998**, *27*, 171–178.

(38) *SAINT-NT*; Bruker AXS Inc.: Madison, WI, 2000.

(39) Sheldrick, G. M. *SADABS 2.0*; Universität Göttingen: Göttingen, Germany, 2000.

(40) *X-Area (version 1.18) and X-RED32 (version 1.04)*; Stoe & Cie: Darmstadt, Germany, 2002.

(41) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.

(42) Sheldrick, G. M. *SHELX-97: Program for the Solution and Refinement of Crystal Structures*; Universität Göttingen: Göttingen, Germany, 1997.