## **ORGANOMETALLICS**

# Reactions of N-Monosubstituted Amidines with AlMe<sub>3</sub> and AlMeCl<sub>2</sub>: Formation of Fused Triazaalane Heterocycles

K. Maheswari and N. Dastagiri Reddy\*

Department of Chemistry, Pondicherry University, Pondicherry 605014, India

#### **Supporting Information**

**ABSTRACT:** Reactions of N-monosubstituted amidines of the formula HN=C(R)-NH(R') (R = Ph, 4-*tert*-butylphenyl, Me; R' = 2,6-diisopropylphenyl, Ph) with AlMe<sub>3</sub> and AlMeCl<sub>2</sub> are reported. All the N-(Dipp)amidines (Dipp = 2,6diisopropylphenyl) react with AlMe<sub>3</sub> in a 1:1 ratio to yield tetrameric aluminum amidinates (1, 2, and 3) in good yields. In these compounds, the amidinate ligand chelates to Al while bridging to another Al. However, when N-phenylamidines are employed, tetracyclic (4–9) and pentacyclic (10) Al–N–C heterocycles are formed. In the case of N-phenylbenzamidine, formation of a hexacyclic Al–N–C heterocycle (11) is observed when a slight excess of AlMe<sub>3</sub> (1:1.2 equiv) is



used. In these compounds, the amidinate ligand coordinates to Al atoms in a bridging fashion. Further, N-(Dipp)acetamidine and N-(Dipp)benzamidine are also treated with AlMeCl<sub>2</sub>. Whereas N-(Dipp)acetamidine affords an ionic 15-membered aluminum amidinate chain (12), N-(Dipp)benzamidine gives a bicyclic heterocycle (13) and the AlCl<sub>3</sub> adduct of N-(Dipp)benzamidine (14). However, from a reaction between N-phenylbenzamidine and AlMeCl<sub>2</sub>, only the AlCl<sub>3</sub> adduct, 15, was isolated. Compounds 3, 4, 6, 8, and 10–15 have been structurally characterized.

#### ■ INTRODUCTION

Aluminum amidinates have been the theme of interest since the discovery of their use as catalysts for polymerization of olefins.<sup>1</sup> It has also been reported that these compounds are good precursors for atomic layer deposition (ALD) of aluminum nitride.<sup>2</sup> There has been a plethora of N,N-disubstituted amidinates of aluminum reported in the literature.<sup>3</sup> Two major synthetic routes for N,N-disubstituted aluminum amidinates are (i) insertion of carbodiimides into Al-C bonds<sup>4</sup> and (ii) condensation reactions of amidines with aluminum reagents.<sup>3</sup> Mononuclear Al amidinates, in which the amidinate ring chelates to Al, are most commonly found as mono(amidinate) complexes and rarely as bis- and tris(amidinate) complexes.<sup>3a,5</sup> Amidinates can also adopt a bridged coordination with Al, leading to multinuclear complexes.<sup>4,5g,6</sup> Chelate versus bridged coordination of amidinates to Al depends on the steric bulk on N atoms. Bulkier substituents favor chelation, and sterically smaller substituents favor bridging. In contrast, N-monosubstituted amidines have not been thoroughly explored for their reactivity toward Al reagents. Having two acidic protons and comparatively less steric bulk, N-monosubstituted amidines are promising motifs for the synthesis of diverse and complex Al-N frameworks. Recently, we reported the synthesis of a tetrameric aluminum amidinate from N-(Dipp)benzamidine (Dipp = 2,6-diisopropylphenyl) and AlMe<sub>3</sub>.<sup>7</sup> In continuation, we explored the reactions of a few N-(Dipp)- and Nphenylamidines with trimethylaluminum and methylaluminum dichloride. Herein, we report the synthesis and structural

characterization of tetrameric four-membered aluminum amidinates and fused six-membered carbaalumazanes (carbon-containing triazaalanes).

#### RESULTS AND DISCUSSION

Recently, we have found that heating an equimolar mixture of N-(Dipp)benzamidine and AlMe<sub>3</sub> gives a tetrameric aluminum amidinate, 1, in good yield (Scheme 1). Because this reaction is





the only example of N-monosubstituted amidines with AlMe<sub>3</sub>, it is interesting to examine whether analogous amidines with

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similar steric bulk react with AlMe<sub>3</sub> in a similar way. N-(Dipp)-4-*tert*-butylbenzamidine and N-(Dipp)acetamidine, which differ from N-(Dipp)benzamidine only at the central carbon atom, have been employed and treated with AlMe<sub>3</sub> at 170 °C for 2 h. In both cases, facile elimination of methane was observed and tetrameric aluminum amidinates (2 and 3 in Scheme 1) were collected in quantitative yields.

The <sup>1</sup>H NMR spectra of 2 and 3, which show two multiplets and four doublets for isopropyl groups, and a singlet for Al–Me group, are quite similar to that of 1. In addition to these resonances, singlets for the 4-*tert*-butyl group (2) and methyl group on the amidinate carbon (3) are also present in the aliphatic region. Single crystals of 3 were grown from hexane solutions and subjected to X-ray analysis. An ORTEP diagram of 3 along with selected bond parameters is given in Figure 1.



Figure 1. Molecular structure of 3. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å]: Al1-N1 1.912(3), Al1-N2 1.917(3), Al1-N7 1.838(3), Al2-N1 1.828(3), Al2-N3 1.911(3), Al2-N4 1.939(3), Al3-N3 1.825(3), Al3-N5 1.901(3), Al3-N6 1.920(3), Al4-N5 1.827(3), Al4-N7 1.904(3), Al4-N8 1.918(3), Al1-C5 1.950(4), Al2-C6 1.947(4), Al3-C7 1.950(4), Al4-C8 1.942(4), C1-N1 1.333(4), C1-N2 1.349(5), C2-N3 1.324(5), C2-N4 1.341(5), C3-N5 1.327(4), C3-N6 1.339(5), C4-N7 1.330(5), C4-N8 1.344(5). Selected bond angles [deg]: N2-C1-N1 112.1(3), N2-Al1-N1 71.05(13), Al1-N2-C1 88.1(2), Al1-N1-C1 88.7(2), N7-Al1-N1 108.62(14), N7-Al1-N2 116.03(14), N7-Al1-C5 117.46(15), N2-Al1-C5 114.01(17), N1-Al1-C5 121.45(19), N4-C2-N3 113.7(3), N3-Al2-N4 70.86(13), Al2-N3-C2 88.5(2), Al2-N4-C2 86.8(2), N3-Al2-N1 108.03(15), N4-Al2-N1 116.56(14), C6-Al2-N1 117.84(16), C6-Al2-N3 119.02(16), C6-Al2-N4 115.73(16).

The molecular structure of 3 is essentially the same as that of  $1.^7$  It is a cyclic tetramer of four-membered aluminum amidinate, and the bond parameters are as with 1. The central eight-membered Al–N ring adopts a puckered boat conformation, and the adjacent Al–Me groups are trans to each other. The N atoms (N2, N4, N6, and N8), which are not part of the eight-membered ring, lie in the mean plane of the eightmembered ring. The average distance of Al atoms from the mean plane is 0.906 Å, and that of N atoms (N1, N3, N4, and N7) of the eight-membered ring is 0.279 Å. Because the Al atoms are in a tetrahedral geometry, the average dihedral angle between the adjacent four-membered rings is as high as 57.8°.

The aforesaid amidines have large Dipp groups on one of the N atoms, and hence, the chelation has been observed. Reducing the steric bulk on the N atom can increase the bite angle and might lead to bridged coordination. Therefore, the Dipp group has been replaced by a phenyl group, and N-phenylbenzamidine, N-phenyl-4-tert-butylbenzamidine, and N-phenylacetamidine have been explored for their reactivity with AlMe<sub>3</sub>. Heating an equimolar mixture of AlMe<sub>3</sub> and N-phenylbenzamidine at 170 °C for 2 h resulted in a solid residue, which, upon recrystallization from a toluene/hexane mixture, yielded a mixture of isomers of a tetracylic triazaalane, 4 and 5 (Scheme 2), in a 4:1 ratio in good yield. Further recrystallizations did not result in separation of these isomers. The <sup>1</sup>H NMR spectrum clearly shows the presence of a mixture. There are two sets of Al-Me peaks (five singlets for 4 and five singlets for 5) and two N-H peaks present in the spectrum, and the intensity of two sets is in a 4:1 ratio.

Only the crystals of 4 were suitable for single-crystal X-ray diffraction studies, and it has been structurally characterized. An ORTEP diagram with selected bond parameters is provided in Figure 2. The molecular structure of 4 shows a tetracylic Al<sub>4</sub>C<sub>4</sub>N<sub>8</sub> framework. Three six-membered Al<sub>2</sub>CN<sub>3</sub> rings, which are fused together like C6 rings in phenylene, form a highly puckered tricyclic structure with Al in the center of the three rings. An amidinate bridge between the central Al atom and one of the Al atoms in the periphery provides the fourth Al<sub>2</sub>CN<sub>3</sub> ring. While Al atoms are in a distorted tetrahedral geometry, all skeletal C and N atoms are three-coordinated in a planar arrangement. Al-N distances vary from 1.8236(18) Å (Al4-N3) to 1.9611(19) Å (Al2-N2) and are as with the Al-N compounds reported in the literature.<sup>3-8</sup> One of the Al atoms (Al4) is connected to four N atoms, and the Al4-N8 bond (1.9097(18) Å), which is perpendicular to the mean plane of the three Al<sub>2</sub>CN<sub>3</sub> rings, is slightly longer than the rest of the Al4-N bonds (Al4-N1 1.8383(18), Al4-N3 1.8236(18), Al4-N5 1.8564(18) Å).

Under similar reaction conditions, N-phenyl-4-tert-butylbenzamidine afforded a residue, which, upon recrystallization from hexane, yielded an isomeric mixture of a tetracyclic amidinate, 6 and 7, in a 3:1 ratio as a first crop. The <sup>1</sup>H NMR spectrum is similar to that of the isomeric mixture of 4 and 5. Two sets of singlets (four in each set) for tert-butyl groups are also observed. Formation of 6 has been further confirmed by singlecrystal X-ray studies. The molecular structure of 6 with selected bond parameters is given in the Supporting Information (Figure S1). The mother liquor afforded a further crop of crystals, whose <sup>1</sup>H NMR spectrum showed an additional set of six resonances with low intensity in the Al-Me region (see the Supporting Information, Figure S4). A thorough single-crystal X-ray analysis of these crystals revealed the presence of a pentacyclic triazaalane 10. The crystal structure of 10 along with selected bond parameters is given in Figure 3. 10 crystallizes in the  $P\overline{1}$  space group, and there are four dianionic amidinate groups and one monoanionic amidinate group involved in the formation of the molecule. The structure is made of five Al<sub>2</sub>CN<sub>3</sub> rings fused together and looks like an extended structure of 6. There are, in total, five Al atoms in the molecule. Two (Al4 and Al2) are connected to four N atoms, and three (Al1, Al3, and Al5) are connected to two C and two N atoms. The Al–N bonds arising from Al4 and Al2 (av. 1.858 Å) are shorter than the rest of the Al–N bonds (av. 1.940 Å) in the molecule. The sum of the bond angles around each skeletal

#### Scheme 2. Reaction of AlMe<sub>3</sub> with N-Phenylamidines





Figure 2. Molecular structure of 4. All hydrogen atoms, except the one on N7, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Al4-N1 1.8383(18), Al4-N3 1.8236(18), Al4-N5 1.8564(18), Al4-N8 1.9097(18), Al1-N1 1.8515(17), Al1-N6 1.9153(18), Al1-N7 1.9029(19), Al1-C5 1.941(2), N7-C4 1.326(3), N8-C4 1.330(3), Al3-C9 1.975(2), Al2-C7 1.957(2), Al2-N3 1.9143(17), Al2-N2 1.9611(19), N2-C1 1.328(3), N1-C1 1.340(2), N4-C2 1.339(3), N3-C2 1.326(3), Al3-N5 1.9120(19), Al3-N4 1.972(2). Selected bond angles [deg]: N1-Al1-N7 100.15(8), N3-Al2-N2 98.93(8), N5-Al3-N4 101.59(8), C2-N3-Al4 123.84(14), N3-C2-N4 122.5(2), C1-N1-Al4 124.02(15), N2-C1-N1 121.58(19), N1-Al1-C5 122.81(9), N3-Al4-N1 109.97(8), Al1-N7-C4 129.00(16), Al2-N2-C1 123.53(14), Al4-N3-Al2 108.43(10), Al4-N5-Al3 110.84(9), N7-C4-N8 120.4(2), N5-Al3-C9 106.05(10), N3-Al2-C7 116.83(10), Al4-N1-Al1 103.81(8), Al4-N8-C4 127.03(15), N1-Al4-N8 106.95(8), N3-Al4-N5 113.45(8).

C and N atom, which is equal to  $\sim$ 360°, suggests that they are in a trigonal-planar geometry.

Similar to *N*-phenylbenzamidine, *N*-phenylacetamidine also reacts with AlMe<sub>3</sub> and gives an isomeric mixture of **8** and **9** in a

4:1 ratio. **8** has been structurally characterized, and the molecular structure along with selected bond parameters is given in the Supporting Information (Figure S2). Formation of a pentacyclic triazaalane, similar to **10**, has not been observed.

In these reactions, among all the tetracyclic compounds, only one type of isomer (4, 6, and 8) has been characterized structurally. Several attempts have been made to isolate the crystals of the other isomer (5, 7, and 9), but they were unsuccessful. However, in the case of *N*-phenyl-4-*tert*butylbenzamidine, we were able to isolate 6 in pure form by fractional crystallization of a mixture of 6 and 7 from hexane. The <sup>1</sup>H NMR spectrum of this isomer (6) shows only one set of peaks (see the Supporting Information, Figure S5).

Interestingly, when a mixture of N-phenylbenzamidine and a slight excess of  $AlMe_3$  (1:1.2) was heated at 170 °C, a hexacyclic Al–N–C heterocycle, 11, was formed in moderate yield (Scheme 3). Large blocks of crystals, which were subjected to X-ray analysis, were grown from toluene. The molecular structure of 11 along with selected bond parameters is provided in Figure 4.

The basic structure of 11 contains a highly puckered benzo[cd]pyrene-type framework made up of five Al<sub>2</sub>CN<sub>3</sub> rings, and a C–N bridge connecting one of the peripheral Al atoms with the central N atom, which makes the structure hexacyclic. C–N bond distances throughout the molecule, except between C12 and N9, are in between single and double bond distances. It is noteworthy that N9, which is connected to three Al atoms, forms the longest C–N bond (1.408(2) Å) of all the amidine/-ate C–N bonds reported in this study. The <sup>1</sup>H NMR spectrum of **11** shows eight singlets of equal intensity ranging from  $\delta$  –3.02 to 0.73 ppm, which can be assigned to eight Al–Me protons.

Further, we investigated the reactions of N-monosubstituted amidines with AlMeCl<sub>2</sub>. An equimolar homogeneous mixture of AlMeCl<sub>2</sub> and N-(Dipp)acetamidine was heated to 170 °C, and the residue was crystallized from toluene at rt to obtain X-ray quality crystals of an acyclic ionic amidinate, **12** (Scheme 4). Formation of ionic species, **12**, is quite surprising, but it has been reproduced consistently. An ionic species, which was formed in low yield when an  $N_i$ N-diisopropylamidine was

**Figure 3.** Molecular structure of **10**. All hydrogen atoms, except the one on N10, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Al1–N1 1.924(3), Al1–N2 1.955(3), Al2–N1 1.863(3), Al2–N3 1.829(3), Al2–N5 1.858(3), Al2–N7 1.885(3), Al3–N3 1.914(3), Al3–N4 1.972(3), Al4–N5 1.833(3), Al4–N6 1.887(3), Al4–N8 1.854(3), Al4–N10 1.859(3), Al5A–N8 1.889(3), Al5A–N9 1.992(3), Al5B–N8 2.013(3), Al5B–N9 2.030(3), N2–C1 1.354(4), N3–C1 1.328(4), N4–C2 1.335(4), N5–C2 1.325(4), C5–N10 1.332(4), N9–C5 1.314(4), N6–C3 1.381(4), N1–C3 1.303(4), N8–C4 1.317(4), N7–C4 1.369(4), Al1–C6 1.964(4), Al1–C7 1.974(4), Al3–C8 1.974(4), Al3–C9 1.960(4), Al5A–C10A 1.9448, Al5A–C11A 1.9660, Al5B–C10B 1.9162, Al5B–C11B 1.9593. Selected bond angles [deg]: N1–Al1–N2 100.64(12), N3–Al3–N4 100.58(12), N8–Al5A–N9 102.82(13), N8–Al5B–N9 97.25(13), N3–Al2–N1 112.00(13), N3–Al2–N5 111.44(13), N1–Al2–N7 110.73(12), N5–Al2–N7 103.46(13), N3–Al2–N7 114.32(12), N5–Al4–N10 120.58(13), N10–Al4–N6 109.66(13), N10–Al4–N8 107.20(13), N3–C1–N2 121.7(3), C1–N2–Al1 122.6(2), Al2–N3–Al3 111.68(15), C2–N4–Al3 126.5(2), N5–C2–N4 123.7(3), N9–C5–N10 120.6(3), C5–N10–Al4 130.0(2), C5–N9–Al5A 129.7(2), C5–N9–Al5B 114.5(2), N8–C4–N7 123.2(3), Al4–N5–Al2 100.39(13), Al2–N1–Al1 110.44(14), Al4–N8–Al5A 118.20(15), Al4–N8–Al5B 107.34(14).

### Scheme 3. Reaction of AlMe<sub>3</sub> with *N*-Phenylbenzamidine in a 1.2:1 Ratio



treated with EtAlCl<sub>2</sub>, has been reported in the literature.<sup>3c</sup> The single-crystal X-ray structure and selected bond parameters of **12** are given in Figure 5. The solid-state structure shows a 15-membered  $Al_3C_4N_8$  amidinate chain, consisting of two amidinate, two amidine, and three AlCl<sub>2</sub> moieties. There is also a chloride ion, which brings the two ends of the chain closer through hydrogen bonding to amidine hydrogens, present in the molecule. Because of the presence of six NH hydrogen bond donors, **12** has the potential to act as an anion receptor. Several compounds having NH groups have been reported to show an anion binding property toward various anions.<sup>9</sup> The <sup>1</sup>H NMR spectrum of **12** in CDCl<sub>3</sub> shows two sets of resonances. One set of resonances is in accordance with the solid-state structure ( $C_2$  symmetric). Another set of peaks suggests an asymmetric structure, which is formed in solution

presumably due to the binding of chloride ion to only one side of the chain (asymmetric binding). Addition of 1 equiv of  $AgBF_4$  to the NMR tube makes the spectrum simpler. Although the peaks related to the  $C_2$  symmetric structure are intact, the other set of peaks reduces to a great extent.

Under similar conditions, N-(Dipp)benzamidine reacted with AlMeCl<sub>2</sub> to give a mixture of a bicyclic triazaalane, 13, and an N-(Dipp)benzamidine adduct of AlCl<sub>3</sub>, 14 (Scheme 5). One of the Al atoms in 13 is bonded to only one Cl, even though there are two Cl atoms on Al in the starting AlMeCl<sub>2</sub>. Formation of 13 requires AlMe<sub>2</sub>Cl, which is presumably formed due to the exchange of Me and Cl during the course of the reaction. To confirm this, a reaction between the N-(Dipp)benzamidine adduct of AlCl<sub>3</sub>, 14, and AlMe<sub>3</sub> was carried out. When a mixture of 14 and AlMe3 was heated to 170 °C for 2 h, 13 was formed in moderate yield (Scheme 6). Formation of 13 was also observed in a reaction between N-(Dipp)benzamidine and AlMe<sub>2</sub>Cl under similar conditions. However, only the AlCl<sub>3</sub> adduct, 15, was isolated from a reaction between N-phenylbenzamidine and AlMeCl<sub>2</sub> (Scheme 7). The compounds 13-15 have been structurally characterized, and ORTEP diagrams with selected bond parameters are given in Figures 6, 7, and S3 (Supporting Information), respectively. Compound 13, which crystallizes in the  $P\overline{1}$  space group, is a bicyclic triazaalane. The Al<sub>2</sub>N<sub>3</sub>C rings are highly puckered and together form a boatlike structure. The <sup>1</sup>H NMR spectrum of 13 in CDCl<sub>3</sub> is in good agreement with the solid-state structure.



Figure 4. Molecular structure of 11. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Al4-C9 1.966(3), Al4-N6 1.9193(19), Al6-N6 1.8656(19), Al6-N8 1.8794(18), N8-C4 1.326(3), N7-C4 1.356(3), Al4-N7 1.9706(19), N6-C3 1.318(3), N5-C3 1.362(3), Al3-N5 1.903(2), Al3-N9 1.9456(18), Al6-N9 1.9962(18), Al3-N4 1.9205(18), N4-C2 1.352(3), N3-C2 1.318(3), Al5-N3 1.8499(18), Al5-N9 1.9641(18), Al3-C8 1.951(2), Al2A-N3 1.939(2), Al2B-N3 1.894(9), Al2A-N2 1.987(2), Al2B-N2 1.974(9), N2-C1 1.345(3), N1-C1 1.324(3), Al5-N1 1.8750(18), Al1-N1 1.8689(18), Al1-N8 1.8728(18), N9-C12 1.408(2), N10-C12 1.298(3), Al1-C5 1.949(2), Al1-N10 1.9829(18). Selected bond angles [deg]: N6-Al6-N8 111.10(8), N8-Al6-N9 102.70(8), N1-Al1-N8 106.89(8), C9-Al4-C10 119.79(12), Al1-N10-C12 124.81(14), N10-C12-N9 119.70(18), Al4-N7-C4 124.99(14), N8-C4-N7 121.26(19), N6-Al4-C9 112.08(10), Al4-N6-C3 125.77(16), Al6-N6-Al4 108.28(9), Al6-N8-C4 114.45(14), Al5-N1-C1 112.45(14), N1-C1-N2 120.60(19), C6A-Al2A-C7A 115.9(2), C6B-Al2B-C7B 119.4(12), N3-Al2A-N2 100.22(10), N3-Al2B-N2 102.3(4), N3-C2-N4 124.23(19), Al6-N6-C3 125.17(15), Al5-N9-Al6 108.95(8), N1-Al5-N9 103.02(8), Al1-N1-Al5 115.40(9), Al1-N8-Al6 114.67(9), N1-Al1-N10 97.22(8), Al5-N3-C2 127.04(15), Al3-N4-C2 131.60(15), Al5-N3-Al2 108.73(10), N6-Al6-N9 102.27(8), Al3-N9-Al6 102.13(8), N5-Al3-N9 104.11(8), Al3-N5-C3 129.56(15), N6-C3-N5 124.7(2), N4-Al3-N9 101.77(8), Al3-N9-Al5 106.96(8).





It can be seen in the crystal structure that one of the methyl groups is oriented toward the center of a phenyl ring and presumably responsible for the appearance of a doublet



**Figure 5.** Molecular structure of **12**. All hydrogen atoms, except those on N atoms, are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Al1–N1 1.8603(15), Al1–Cl1 2.1243(8), N1–Cl 1.323(2), N2–Cl 1.333(2), Al2–N2 1.8867(16), Al2–Cl3 2.1083(7), Al2–N3 1.8509(17), C2–N3 1.318(2), C2–N4 1.321(2). Selected bond angles [deg]: N1–Al1–N1' 113.20(10), Cl1–Al1–Cl1' 115.10(6), Al–N1–Cl 132.27(13), N1–C1–N2 123.58(16), Al2–N2–Cl 127.18(12), N3–Al2–N2 102.09(7), Al2–N3–C2 134.27(13), N3–C2–N4 119.96(17), Cl3–Al2–Cl2 109.67(3).

Scheme 5. Reaction of AlMeCl<sub>2</sub> with N-(Dipp)benzamidine



Scheme 6. Reaction of AlMe<sub>3</sub> with *N*-(Dipp)benzamidine•AlCl<sub>3</sub> Adduct



resonance at 0.20 ppm, which is quite high field for methyl protons of the isopropyl group.

In compounds 1-15, the amidinate or amidine ligands show several coordination modes (Figure 8). Mono- and dianionic N-monosubstituted amidinates show two and three types of coordination modes, respectively, whereas the neutral amidine



Scheme 7. Reaction of AlMeCl<sub>2</sub> with N-Phenylbenzamidine

Figure 6. Molecular structure of 13. All hydrogens except on N atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: N2–C1 1.342(3), N3–C1 1.329(2), Al2–N3 1.8580(17), Al2–N1 1.8668(18), Al1–N1 1.8872(18), Al1–N2 1.8881(18), Al1–Cl1 2.1304(9), Al3–Cl5 2.0993(9), N1–C3 1.304(3), Al3–N3 1.8728(18), Al3–N4 1.9253(18), N4–C2 1.328(3), N5–C2 1.332(3), Al2–N5 1.8642(18), Al2–Cl3 2.1234(8). Selected bond angles [deg]: Al1–N1–C3 122.70(14), Al1–N2–C1 122.06(14), Al2–N1–Al1 110.50(9), N3–Al2–N1 106.12(8), N3–Al3–N4 103.81(8), N1–Al1–N2 110.28(8), N3–C1–N2 121.74(18), Al2–N1–C3 125.74(14), Al2–N3–C1 123.95(14), N2–Al1–Cl1 110.03(6), N3–Al3–Cl5 116.27(6), N3–Al2–N5 105.24(8), Al2–N5–C2 132.83(14), N4–C2–N5 119.13(18), Al3–N4–C2 119.37(14), Al2–N3–Al3 109.34(8), N1–C3–N6 123.02(19).

shows only one type of coordination mode. Compounds 1–3 contain the amidinate in a  $\mu - \eta^1, \eta^2$  bridge mode, and in 11, one of the benzamidinate units bridges four Al atoms in a  $\mu_4 - \eta^1, \eta^3$  fashion. Three different coordination modes  $(\mu_3 - \eta^1, \eta^2; \mu - \eta^0, \eta^2; \text{ and } \mu - \eta^1, \eta^1)$  have been observed in 13, which contains three amidinate ligands and three Al atoms. As expected, the amidinate N–C–N bond angle in the  $\mu - \eta^1, \eta^2$  bridge mode is lower (e.g., av. N–C–N bond angle in 1 is 112.79°) than that found in other coordination modes, which is around 120°. In the  $\mu_4 - \eta^1, \eta^3$  bonding mode, which is found only in 11, the amidinate C–N and C–N' distances vary to a greater extent (C12–N9 1.408(2) and C12–N10 1.298(3) Å) and almost represent single and double bonds, as depicted in Figure 8. In the rest of the coordination modes, these bonds fall in between C–N single and double distances.

#### CONCLUSION

Unlike N,N-disubstituted amidines, when treated with AlMe<sub>3</sub>, N-monosubstituted amidines give complex Al–N–C frame-



Figure 7. Molecular structure of 14. All hydrogens except on N atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å]: Al1–N1 1.8735(15), N1–C1 1.316(2), N2–C1 1.327(2), Al1–Cl1 2.1263(7). Selected bond angles [deg]: N1–C1–N2 121.57(15), Al1–N1–C1 136.35(12), N1–Al1–Cl1 108.40(5).



Figure 8. Coordination modes of N-monosubstituted amidinates/ amidines with Al observed in this study.

works. In the case of the amidines having a Dipp group on the N atom, formation of tetrameric four-membered AlN<sub>2</sub>C rings has been observed exclusively. When a less-bulky group, phenyl, is present, fused six-membered Al<sub>2</sub>N<sub>3</sub>C rings have been formed. These six-membered heterocycles, fused into bi-, tetra-, penta-, and hexacyclic frameworks, are the first examples for polycyclic carbatriazaalanes. Coordination modes of N-monosubstituted amidinates, observed in this study, can provide an insight into the coordination behavior of these amidinates.

#### EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under a  $N_2$  atmosphere using a Schlenk line and a glovebox. Trimethylaluminum, methylaluminum dichloride, dimethylaluminum chloride, 4-*tert*-butylbenzonitrile, acetonitrile, and 2,6-diisopropylaniline were procured from Aldrich and used as received. *N*-(Dipp)benzamidine<sup>7</sup> and N-phenylbenzamidine<sup>10</sup> were prepared by following literature procedures. Hexane and toluene (from Na/benzophenone ketyl) were distilled fresh as and when required. <sup>1</sup>H and <sup>13</sup>C spectra were recorded on a Bruker 400 MHz instrument. Elemental analyses were performed using an Elementar Vario EL III analyzer.

**Structural Determination for 3, 4, 6, 8, and 10–15.** The single crystals of 3, 4, 6, 8, and 10–15 were mounted on a glass fiber in paraffin oil and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. Data collection was performed on an OXFORD XCALIBUR diffractometer, equipped

#### **Organometallics**

#### Table 1. Crystal Data for Compounds 3, 4, and 10-14

	$3 \cdot C_7 H_8$	$4 \cdot C_7 H_8$		$10.1/2C_6H_{14} \& 1/2C_5H_{10}$	$11.2C_7H_8$
empirical formula	C <sub>127</sub> H <sub>192</sub> Al <sub>8</sub> N <sub>16</sub>	$C_{64}H_{64}Al_4N_8$		C <sub>96 50</sub> H <sub>122</sub> Al <sub>5</sub> N <sub>10</sub>	C <sub>87</sub> H <sub>90</sub> Al <sub>6</sub> N <sub>10</sub>
formula wt	2158.81	1053.15		1556.94	1437.57
temp (K)	293(2)	150(2)		293(2)	150(2)
cryst syst	triclinic	triclinic		triclinic	monoclinic
space group	$P\overline{1}$	$P\overline{1}$		$P\overline{1}$	C2/c
a (Å)	18.5489(3)	14.1228(6)		15.0411(4)	42.1990(12)
b (Å)	18.6181(3)	14.1451(7)		15.6755(5)	14.0190(3)
c (Å)	21.6897(4)	16.4352(8)		21.7746(6)	27.7014(8)
$\alpha$ (deg)	90.704(2)	94.097(4)		89.763(2)	90
$\beta$ (deg)	105.772(2)	114.481(4)		77.295(2)	101.977 (3)
$\gamma$ (deg)	103.897(2)	101.097(4)		87.019(2)	90
$V(Å^3)$	6973.3(2)	2889.9(2)		5001.3(2)	16031.1(7)
Z	2	2		2	8
$\rho_{\text{calad}} (\text{mg m}^{-3})$	1.028	1.210		1.034	1.191
$\mu (\text{mm}^{-1})$	0.107	0.128		0.101	0.131
F(000)	2340	1112		1672	6080
cryst size (mm)	$0.55 \times 0.45 \times 0.25$	$0.40 \times 0.26 \times 0.12$		$0.14 \times 0.12 \times 0.12$	$0.18 \times 0.09 \times 0.06$
$\theta$ range (deg)	2.75-25.00	2.62-29.33		2.51-25.00	2.64-29.32
no. of collected/unique reflns	64251/24508 (R(int) = 0.0531)	24141/13281 ( <i>R</i> (int) 0.0533)	=	41481/17578 (R(int) = 0.0576)	38473/18601 (R(int) = 0.0317)
no. of data/restraints/params	24508/6/1354	13281/0/691		17578/30/957	18601/104/907
R1, wR2 $(I > 2\sigma(I))^a$	0.0743, 0.2259	0.0512, 0.0921		0.0755, 0.2118	0.0536, 0.1420
R1, wR2 (all data) <sup><math>a</math></sup>	0.1110, 0.2540	0.1278, 0.1043		0.1221, 0.2393	0.0924, 0.1546
GOF	1.042	0.837		1.037	1.030
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}$ (e Å <sup>-3</sup> )	1.725/-0.534	0.305/-0.323		0.843/-0.483	0.699/-0.737
	10 C II				
	12·C <sub>7</sub> H	8		$13 \cdot 2C_7 H_8$	14
empirical formula	C <sub>63</sub> H <sub>94</sub> Al <sub>3</sub> Cl <sub>7</sub> N <sub>8</sub>	8	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C	13·2C <sub>7</sub> H <sub>8</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub>
empirical formula formula wt	C <sub>63</sub> H <sub>94</sub> Al <sub>3</sub> Cl <sub>7</sub> N <sub>8</sub> 1292.55	-8 ( ]	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63	13·2C <sub>7</sub> H <sub>8</sub> l <sub>3</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73
empirical formula formula wt temp (K)	$12 C_7 H$ $C_{63}H_{94}Al_3Cl_7N_8$ 1292.55 150(2)	8 ( ] ]	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63 150(2)	13·2C <sub>7</sub> H <sub>8</sub> l <sub>5</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73 150(2)
empirical formula formula wt temp (K) cryst syst	$12 C_7 H$ $C_{63}H_{94}Al_3Cl_7N_8$ 1292.55 150(2) monoclinic	8 [] ] t	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63 150(2) triclinic	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73 150(2) triclinic
empirical formula formula wt temp (K) cryst syst space group	$\frac{12\cdot C_{7}H}{C_{63}H_{94}Al_{3}Cl_{7}N_{8}}$ 1292.55 150(2) monoclinic C2/c	8 ( ] ] ] t	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63 150(2) triclinic P <del>1</del>	13·2C <sub>7</sub> H <sub>8</sub> l <sub>3</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73 150(2) triclinic PI
empirical formula formula wt temp (K) cryst syst space group a (Å)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \end{array}$	8 1 1 1 1 1 1	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63 150(2) triclinic P <del>I</del> 14.8034(5)	13·2C <sub>7</sub> H <sub>8</sub> l <sub>3</sub> N <sub>6</sub>	$     \begin{array}{r} 14 \\     C_{19}H_{24}AlCl_{3}N_{2} \\     413.73 \\     150(2) \\     triclinic \\     P\overline{1} \\     8.2030(4) \end{array} $
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \end{array}$	8 0 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6)	13·2C <sub>7</sub> H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73 150(2) triclinic Pī 8.2030(4) 9.3135(4)
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A l_3 C l_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \end{array}$	8 0 1 1 1 1 1 1 1 1 1 1	C <sub>71</sub> H <sub>84</sub> Al <sub>3</sub> C 1279.63 150(2) triclinic P <u>1</u> 14.8034(5) 15.4522(6) 17.9574(6)	13·2C <sub>7</sub> H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	14 C <sub>19</sub> H <sub>24</sub> AlCl <sub>3</sub> N <sub>2</sub> 413.73 150(2) triclinic Pī 8.2030(4) 9.3135(4) 13.9156(6)
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) $\alpha$ (deg)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A l_3 C l_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \end{array}$	8 ( ] ] t ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ]	$C_{71}H_{84}AI_3C$ 1279.63 150(2) triclinic $P\overline{I}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3)	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A l_3 C l_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \end{array}$	8 ( ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ]	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3)	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg) $\gamma$ (deg)	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \end{array}$	8 ( ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ]	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3)	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \\ 89.708(4) \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> )	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \end{array}$	8 ( ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ]	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2)	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \\ 89.708(4) \\ 1060.14(8) \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \\ 4 \end{array}$	8 ( ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ] ]	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2) 2	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \\ 89.708(4) \\ 1060.14(8) \\ 2 \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> )	$\begin{array}{c} 12 \cdot C_7 H \\ C_{63} H_{94} A I_3 C I_7 N_8 \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \\ 4 \\ 1.169 \end{array}$	8 () 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2) 2 1.214	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \\ 89.708(4) \\ 1060.14(8) \\ 2 \\ 1.296 \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> )	$\begin{array}{c} 12\cdot C_7H\\ C_{63}H_{94}Al_3Cl_7N_8\\ 1292.55\\ 150(2)\\ monoclinic\\ C2/c\\ 26.8732(7)\\ 15.3876(3)\\ 19.2603(9)\\ 90\\ 112.737(4)\\ 90\\ 7345.5(4)\\ 4\\ 1.169\\ 0.347\end{array}$	8 () 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2) 2 1.214 0.289	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	14 $C_{19}H_{24}AlCl_3N_2$ 413.73         150(2)         triclinic $P\overline{1}$ 8.2030(4)         9.3135(4)         13.9156(6)         85.993(4)         88.458(4)         89.708(4)         1060.14(8)         2         1.296         0.478
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000)	$\begin{array}{c} C_{63}H_{94}Al_3Cl_7N_8\\ 1292.55\\ 150(2)\\ monoclinic\\ C2/c\\ 26.8732(7)\\ 15.3876(3)\\ 19.2603(9)\\ 90\\ 112.737(4)\\ 90\\ 7345.5(4)\\ 4\\ 1.169\\ 0.347\\ 2744\\ \end{array}$	8 ( 1 1 1 1 1 1 1 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352	13·2C7H <sub>8</sub> 1 <sub>5</sub> N <sub>6</sub>	$\begin{array}{c} 14 \\ C_{19}H_{24}AlCl_{3}N_{2} \\ 413.73 \\ 150(2) \\ triclinic \\ P\overline{1} \\ 8.2030(4) \\ 9.3135(4) \\ 13.9156(6) \\ 85.993(4) \\ 88.458(4) \\ 89.708(4) \\ 1060.14(8) \\ 2 \\ 1.296 \\ 0.478 \\ 432 \end{array}$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm)	$\begin{array}{c} C_{63}H_{94}Al_{3}Cl_{7}N_{8}\\ 1292.55\\ 150(2)\\ monoclinic\\ C2/c\\ 26.8732(7)\\ 15.3876(3)\\ 19.2603(9)\\ 90\\ 112.737(4)\\ 90\\ 7345.5(4)\\ 4\\ 1.169\\ 0.347\\ 2744\\ 0.40 \times 0.32 \times 0.24\end{array}$	8 ( 1 1 1 1 1 1 1 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 108.308(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$	13·2C <sub>7</sub> H <sub>8</sub> l <sub>5</sub> N <sub>6</sub>	14 $C_{19}H_{24}AlCl_3N_2$ 413.73         150(2)         triclinic $P\overline{1}$ 8.2030(4)         9.3135(4)         13.9156(6)         85.993(4)         88.458(4)         89.708(4)         1060.14(8)         2         1.296         0.478         432         0.22 × 0.11 × 0.03
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empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm) $\theta$ range (deg) no. of collected/unique re	$\begin{array}{c} & C_{63}H_{94}Al_3Cl_7N_8\\ 1292.55\\ 150(2)\\ monoclinic\\ C2/c\\ 26.8732(7)\\ 15.3876(3)\\ 19.2603(9)\\ 90\\ 112.737(4)\\ 90\\ 7345.5(4)\\ 4\\ 1.169\\ 0.347\\ 2744\\ 0.40 \times 0.32 \times 0.24\\ 2.64-28.76\\ flns\\ 28443/8552 \left(R(ini)\right)\\ \end{array}$	s ( 1 1 1 1 1 1 1 1 1 1 1 1 1	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$ 2.73-29.35 29327/1603	$13 \cdot 2C_7 H_8$ $1_5 N_6$ $3 \times 0.20$ 36 (R(int) = 0.0371)	14 $C_{19}H_{24}AlCl_3N_2$ 413.73150(2)triclinic $P\overline{1}$ 8.2030(4)9.3135(4)13.9156(6)85.993(4)88.458(4)89.708(4)1060.14(8)21.2960.4784320.22 × 0.11 × 0.032.72-29.318527/4843 ( $R(int) = 0.0289$ )
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empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm) $\theta$ range (deg) no. of collected/unique re no. of data/restraints/para $R1$ , $wR2$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	$\begin{array}{c} & C_{63}H_{94}Al_3Cl_7N_8\\ 1292.55\\ 150(2)\\ monoclinic\\ C2/c\\ 26.8732(7)\\ 15.3876(3)\\ 19.2603(9)\\ 90\\ 112.737(4)\\ 90\\ 7345.5(4)\\ 4\\ 1.169\\ 0.347\\ 2744\\ 0.40 \times 0.32 \times 0.24\\ 2.64-28.76\\ flns\\ 28443/8552\ (R(intimes)\\ 8552/68/394\\ 0.0461, 0.1164\\ \end{array}$	s = 0.0313)	$C_{71}H_{84}AI_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$ 2.73-29.35 29327/1603 16036/0/78 0.0467, 0.12	$13 \cdot 2C_7 H_8$ $l_5 N_6$ $5 \times 0.20$ $36 (R(int) = 0.0371)$ $30$ $221$	14 $C_{19}H_{24}AlCl_3N_2$ 413.73150(2)triclinic $P\overline{1}$ 8.2030(4)9.3135(4)13.9156(6)85.993(4)88.458(4)89.708(4)1060.14(8)21.2960.4784320.22 × 0.11 × 0.032.72-29.318527/4843 (R(int) = 0.0289)4843/0/2300.0355, 0.0789
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm) $\theta$ range (deg) no. of collected/unique re no. of data/restraints/para $R1$ , $wR2$ ( $I > 2\sigma(I)$ ) <sup>a</sup> R1, $wR2$ (all data) <sup>a</sup>	$\begin{array}{c} & C_{63}H_{94}Al_{3}Cl_{7}N_{8} \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \\ 4 \\ 1.169 \\ 0.347 \\ 2744 \\ 0.40 \times 0.32 \times 0.24 \\ 2.64-28.76 \\ flns \\ 28443/8552 \left( R(int ms \\ 8552/68/394 \\ 0.0461, 0.1164 \\ 0.0646, 0.1283 \\ \end{array} \right)$	s = 0.0313)	$C_{71}H_{84}AI_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$ 2.73-29.35 29327/1603 16036/0/78 0.0467, 0.12 0.0818, 0.13	$13 \cdot 2C_7 H_8$ $l_5 N_6$ $5 \times 0.20$ $36 (R(int) = 0.0371)$ $30$ $221$ $312$	14 $C_{19}H_{24}AlCl_3N_2$ 413.73150(2)triclinic $P\overline{1}$ 8.2030(4)9.3135(4)13.9156(6)85.993(4)88.458(4)89.708(4)1060.14(8)21.2960.4784320.22 × 0.11 × 0.032.72-29.318527/4843 ( $R(int) = 0.0289$ )4843/0/2300.0355, 0.07890.0619, 0.0852
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm) $\theta$ range (deg) no. of collected/unique re no. of data/restraints/para $R1$ , $wR2$ ( $I > 2\sigma(I)$ ) <sup>a</sup> R1, $wR2$ (all data) <sup>a</sup> GOF	$\begin{array}{c} & C_{63}H_{94}Al_{3}Cl_{7}N_{8} \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \\ 4 \\ 1.169 \\ 0.347 \\ 2744 \\ 0.40 \times 0.32 \times 0.24 \\ 2.64-28.76 \\ flns \\ 28443/8552 (R(int ms \\ 8552/68/394 \\ 0.0461, 0.1164 \\ 0.0646, 0.1283 \\ 1.042 \end{array}$	$s = \frac{1}{2}$	$C_{71}H_{84}Al_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$ 2.73-29.35 29327/1603 16036/0/78 0.0467, 0.13 0.0818, 0.15 0.969	$13 \cdot 2C_7 H_8$ $1_5 N_6$ $3 \times 0.20$ $36 (R(int) = 0.0371)$ $30$ $221$ $312$	14 $C_{19}H_{24}AlCl_3N_2$ 413.73150(2)triclinic $P\overline{1}$ $8.2030(4)$ $9.3135(4)$ $13.9156(6)$ $85.993(4)$ $88.458(4)$ $89.708(4)$ $1060.14(8)$ 2 $1.296$ $0.478$ $432$ $0.22 \times 0.11 \times 0.03$ $2.72-29.31$ $8527/4843 (R(int) = 0.0289)$ $4843/0/230$ $0.0355, 0.0789$ $0.0619, 0.0852$ $0.984$
empirical formula formula wt temp (K) cryst syst space group a (Å) b (Å) c (Å) a (deg) $\beta$ (deg) $\gamma$ (deg) V (Å <sup>3</sup> ) Z $\rho_{calcd}$ (mg m <sup>-3</sup> ) $\mu$ (mm <sup>-1</sup> ) F(000) cryst size (mm) $\theta$ range (deg) no. of collected/unique re no. of data/restraints/para $R1$ , $wR2$ ( $I > 2\sigma(I)$ ) <sup>a</sup> R1, $wR2$ (all data) <sup>a</sup> GOF $\Delta \rho_{max}/\Delta \rho_{min}$ (e Å <sup>-3</sup> )	$\begin{array}{c} & C_{63}H_{94}Al_{3}Cl_{7}N_{8} \\ 1292.55 \\ 150(2) \\ monoclinic \\ C2/c \\ 26.8732(7) \\ 15.3876(3) \\ 19.2603(9) \\ 90 \\ 112.737(4) \\ 90 \\ 7345.5(4) \\ 4 \\ 1.169 \\ 0.347 \\ 2744 \\ 0.40 \times 0.32 \times 0.24 \\ 2.64-28.76 \\ flns \\ 28443/8552 (R(int) \\ ms \\ 8552/68/394 \\ 0.0461, 0.1164 \\ 0.0646, 0.1283 \\ 1.042 \\ 0.599/-0.417 \end{array}$	$s = \frac{1}{2}$	$C_{71}H_{84}AI_3C$ 1279.63 150(2) triclinic $P\overline{1}$ 14.8034(5) 15.4522(6) 17.9574(6) 105.641(3) 104.256(3) 3500.6(2) 2 1.214 0.289 1352 $0.28 \times 0.28$ 2.73-29.35 29327/1603 16036/0/78 0.0467, 0.12 0.0818, 0.13 0.969 0.566/-0.8	$13 \cdot 2C_7 H_8$ $1_5 N_6$ $5 \times 0.20$ $36 (R(int) = 0.0371)$ $30$ $221$ $312$ $13$	14 $C_{19}H_{24}AlCl_3N_2$ 413.73150(2)triclinic $P\overline{1}$ 8.2030(4)9.3135(4)13.9156(6)85.993(4)88.458(4)89.708(4)1060.14(8)21.2960.4784320.22 × 0.11 × 0.032.72-29.318527/4843 ( $R(int) = 0.0289$ )4843/0/2300.0355, 0.07890.0619, 0.08520.9840.326/-0.245

with a CCD area detector, using graphite-monochromated Mo K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation and a low-temperature device. All calculations were performed using SHELXS-97 and SHELXL-97.<sup>11</sup> The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full-matrix least-squares refinement (against  $F^2$ ). All non-hydrogen atoms were refined anisotropically (except one of the *tert*-Bu groups in **6** and most of the solvent molecules). One of the *tert*-Bu groups in **6**, one AlMe<sub>2</sub> group and one *tert*-Bu group in **10**, and four carbon atoms of a phenyl group and one

AlMe<sub>2</sub> group in **11** were disordered. These groups were modeled by using occupancy factors, SADI and EADP instructions. In **6** and **10**, solvent molecules were severely disordered and the SQUEEZE program was used to eliminate the residues. Details of refinement of the disordered groups and solvent molecules are given in the Supporting Information. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the Xray structures showed no significant peaks. All the data sets were collected to  $2\Theta$  values > 50°, but they were cut off to  $2\Theta = 50^{\circ}$  during the refinement. Relevant data concerning crystallographic data, data collection, and refinement details for 3, 4, and **10–14** are summarized in Table 1, and those for 6, 8, and **15** are given in Table S1 (see the Supporting Information). Crystallographic data (excluding structure factors) for the structures reported in this paper have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 821219– 821225, 831925, 831926, and 836071. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

Synthesis of N-Phenyl-4-tert-butylbenzamidine. To a mixture of aniline (2.99 g, 32.21 mmol) and 4-tert-butylbenzonitrile (5.12 g, 32.20 mmol) was added AlCl<sub>3</sub> (4.28 g, 32.23 mmol) at 0 °C. The mixture was stirred at this temperature for 10 min and heated at 180 °C for 30 min. The molten mixture was poured into a thoroughly mixed solution of 1 mL of HCl and 80 mL of water. To this mixture were added 60 mL of CH<sub>2</sub>Cl<sub>2</sub> and 20 mL of saturated NaHCO<sub>3</sub>, and the organic layer was separated. The aqueous layer was washed three times with CH<sub>2</sub>Cl<sub>2</sub>. All the organic layers were combined and dried over Na2SO4. After removal of volatiles using a rotary evaporator, a viscous liquid was obtained. This was dissolved in 60 mL of hexane and kept in the refrigerator to obtain a colorless crystalline material (4.93 g, 61%). The product was further purified by vacuum sublimation (0.05 mbar, 120 °C). mp: 150-151 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.35 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 4.81 (s, 2H, NH), 6.99 (m, 2H, ArH), 7.06 (m, 1H, ArH), 7.35 (m, 2H, ArH), 7.46 (m, 2H, ArH), 7.79 (m, 2H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 31.35, 34.95, 121.83, 123.05, 125.58, 126.66, 129.61, 133.00, 150.12, 154.09, 181.57.

**Synthesis of N-(Dipp)-4-***tert***-butylbenzamidine.** The same procedure as mentioned for the synthesis of *N*-phenyl-4-*tert*-butylbenzamidine, except for the reaction time of 2 h in this case, was followed, using 2,6-diisopropylaniline (5.12 g, 28.92 mmol), 4-*tert*-butylbenzonitrile (4.60 g, 28.89 mmol), and AlCl<sub>3</sub> (3.84 g, 28.87 mmol). The product was further purified by vacuum sublimation (0.05 mbar, 160 °C). Yield: 57% (5.49 g). mp: 193–194 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.19 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>), 3.06 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.60 (s, 2H, NH), 7.09 (m, 1H, ArH), 7.17 (m, 2H, ArH), 7.52 (m, 2H, ArH), 7.89 (m, 2H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  23.72, 23.85, 28.31, 31.39, 34.98, 123.47, 125.67, 126.63, 132.94, 139.48, 144.36, 153.24, 153.93.

Synthesis of N-Phenylacetamidine. This procedure has been adopted from the literature.<sup>12</sup> To a mixture of aniline (15.36 g, 165.16 mmol) and acetonitrile (6.77 g, 165.16 mmol) was added AlCl<sub>3</sub> (21.96 g, 165.16 mmol) at 0 °C over a period of 30 min. The mixture was stirred at this temperature for 10 min and heated at 100 °C for 30 min. After the dropwise addition of water to the cooled crude product, the amidine base was liberated by the addition of NaOH solution (24 g in 160 mL of water) and the mixture was extracted three times with CH<sub>2</sub>Cl<sub>2</sub>. All the organic layers were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the volatiles using a rotary evaporator, a dark brown oil was obtained. Vacuum distillation of this crude product gave a yellow oil, which was solidified after a day. Yield: 76% (16.72 g). mp: 61–63 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 2.05 (s, 3H, CH<sub>3</sub>), 4.56 (s, 2H, NH), 6.85 (m, 2H, ArH), 6.99 (m, 1H, ArH), 7.28 (m, 2H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 22.99, 115.15, 121.92, 122.79, 129.35, 149.75.

**Synthesis of** *N***-(Dipp)acetamidine.** The same procedure as mentioned for the synthesis of *N*-phenylacetamidine was followed, using 2,6-diisopropylaniline (9.31 g, 52.54 mmol), acetonitrile (2.15 g, 52.54 mmol), and AlCl<sub>3</sub> (6.98 g, 52.54 mmol). The crude product was recrystallized from hexane, and the crystalline material was further purified by vacuum sublimation (0.05 mbar, 100 °C). Yield: 73% (8.35 g). mp: 120–121 °C (reported 118–120 °C).<sup>13 1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.16 (m, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.12 (s, 3H, CH<sub>3</sub>), 2.99 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 4.28 (s, 2H, NH), 7.03 (m, 1H, ArH), 7.10 (m, 2H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  22.11, 23.86, 28.08, 122.99, 123.39, 139.66, 143.89, 153.46.

General Procedure for the Reaction of Amidines with AlMe<sub>3</sub>. A mixture of amidine (1 equiv) and trimethylaluminum (1 equiv) was taken in a Schlenk flask and heated to 170 °C for 2 h. After the reaction mixture was cooled to room temperature, the residue was dissolved either in hexane or in a toluene–hexane mixture and filtered using Celite.

**N**-(Dipp)-4-*tert*-butylbenzamidine with AlMe<sub>3</sub>. N-(Dipp)-4*tert*-butylbenzamidine (0.49 g, 1.48 mmol), AlMe<sub>3</sub> (0.74 mL, 2 M in toluene, 1.48 mmol), hexane (20 mL). The filtrate afforded colorless crystals of **2** in quantitative yield. mp: 242–245 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  –0.69 (s, 12H, AlMe), 0.66 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.93 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.01 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.21 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.56 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.95 (m, 8H, ArH), 6.99 (m, 4H, ArH), 7.05 (m, 12H, ArH), 7.12 (m, 4H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ –10.73, 23.13, 23.58, 25.76, 25.84, 27.86, 28.23, 31.16, 34.77, 123.50, 123.66, 124.87, 125.18, 128.30, 132.60, 139.36, 144.08, 144.61, 153.31, 180.14. Anal. Calcd for C<sub>102</sub>H<sub>132</sub>Al<sub>4</sub>N<sub>8</sub>: C, 77.63; H, 8.43; N, 7.10. Found: C, 77.50; H, 8.64; N, 7.17.

*N*-(Dipp)acetamidine with AlMe<sub>3</sub>. *N*-(Dipp)acetamidine (0.83 g, 3.81 mmol), AlMe<sub>3</sub> (1.90 mL, 2 M in toluene, 3.80 mmol), hexane (30 mL). The filtrate afforded a crystalline material of compound **3** in quantitative yield. mp: 240 °C (dec). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  –0.45 (s, 12H, AlMe), 1.11 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.16 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (m, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.76 (s, 12H, CH<sub>3</sub>), 3.19 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.31 (m, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.13 (m, 2H, ArH), 7.15 (m, 4H, ArH), 7.18 (m, 6H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  –11.65, 20.29, 23.75, 23.87, 25.07, 25.24, 27.79, 28.23, 123.43, 123.58, 125.74, 139.10, 144.63, 145.20, 182.00. Anal. Calcd for C<sub>60</sub>H<sub>92</sub>Al<sub>4</sub>N<sub>8</sub>: C, 69.74; H, 8.97; N, 10.84. Found: C, 69.62; H, 8.93; N, 10.86.

N-Phenylbenzamidine with AlMe<sub>3</sub> (1:1 Ratio). N-Phenylbenzamidine (0.25 g, 1.27 mmol), AlMe3 (0.64 mL, 2 M in toluene, 1.28 mmol), toluene (10 mL), hexane (4 mL). The filtrate afforded a mixture of crystals of  $4 \cdot C_7 H_8$  and 5 in a 4:1 ratio (0.24 g, 78%). Removing the solvents from the mother liquor gave a crystalline residue (0.06 g), which was found to be a mixture of 4 and 5 with a slight amount of impurities. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): the intensity of peaks for 4 and 5 are in a 4:1 ratio.  $\delta$  -2.45 (s, 3H, AlMe (4)), -2.29 (s, 3H, AlMe (5)), -2.14 (s, 3H, AlMe (4) and 3H, AlMe (5)), -2.10 (s, 3H, AlMe (4)), -1.96 (s, 3H, AlMe (5)), -0.45 (s, 3H, AlMe (5)), -0.44 (s, 3H, AlMe (4) and 3H, AlMe (5)), -0.31 (s, 3H, AlMe (4)), 2.36 (s, 3H, CH<sub>3</sub>(tol.)), 5.36 (s, 1H, NH (4)), 5.68 (s, 1H, NH (5)), 6.09 (d, 2H, ArH (4)), 6.67-7.40 (m, 37H, ArH (4), 5H, ArH (tol) and 40H (5)), 7.63 (d, 1H, ArH (4)). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ -10.74, -9.16, -8.17, -7.80, -6.65, 21.62, 123.57, 124.25, 125.05, 125.45, 126.40, 127.04, 127.15, 127.19, 127.50, 127.56, 127.67, 127.68, 127.83, 127.91, 128.00, 128.19, 128.26, 128.30, 128.38, 128.43, 128.46, 128.68, 128.97, 128.19, 129.35, 129.51, 137.30, 137.75, 138.03, 139.64, 139.81, 140.56, 140.83, 140.90, 141.40, 144.46, 145.18, 146.08, 146.13, 147.25, 147.48, 147.78, 147.92, 175.86, 176.62, 176.74, 177.11, 178.53, 178.74, 179.67, 180.98. A sample for elemental analysis was prepared by heating a mixture of 4 and 5 at 80 °C for 2 h under high vacuum. Anal. Calcd for C57H56Al4N8: C, 71.24; H, 5.87; N, 11.66. Found: C, 71.02; H, 5.93; N, 11.70.

N-Phenyl-4-tert-butylbenzamidine with AlMe<sub>3</sub>. N-Phenyl-4tert-butylbenzamidine (0.26 g, 1.03 mmol), AlMe<sub>3</sub> (0.50 mL, 2 M in toluene, 1.00 mmol), hexane (15 mL). The filtrate was allowed to evaporate slowly under nitrogen to obtain colorless crystals of 6 and 7 (0.25 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): the intensity of peaks for 6 and 7 are in a 3:1 ratio.  $\delta$  -2.49 (s, 3H, AlMe (6)), -2.32 (s, 3H, AlMe (7)), -2.22 (s, 3H, AlMe (7)), -2.17 (s, 3H, AlMe (6)), -2.16 (s, 3H, AlMe (6)), -2.02 (s, 3H, AlMe (7)), -0.44 (s, 6H, AlMe (6 and 7)), -0.40 (s, 3H, AlMe (7)), -0.33 (s, 3H, AlMe (6)), 1.09 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (**6**)), 1.13 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (7)), 1.17 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (7)), 1.18 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (7)), 1.19 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (6)), 1.21 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (6)), 1.27 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (6)), 1.30 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub> (7)), 5.33 (s, 1H, NH (6)), 5.65 (s, 1H, NH (7)), 6.12 (d, 2H, ArH (6)), 6.65–7.60 (set of multiplets, 32H, ArH (6) and 36H, ArH (7)). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  –10.86, –9.24, –8.13, –7.77, –6.50, 11.59, 18.93, 20.60, 20.87, 22.81, 25.44, 27.08, 27.83, 29.22, 30.92,

31.09, 31.21, 31.25, 31.31, 34.46, 34.54, 34.64, 34.68, 34.83, 34.85, 34.97, 36.24, 41.51, 123.30, 123.81, 124.01, 124.20, 124.24, 124.72, 125.20, 126.18, 127.08, 127.42, 127.52, 127.60, 127.70, 128.12, 128.38, 128.51, 128.93, 129.15, 129.27, 134.60, 137.01, 138.75, 144.66, 146.43, 147.55, 147.80, 148.09, 150.45, 151.10, 151.13, 152.73, 175.88, 176.36, 176.99, 178.71, 178.92, 179.72, 180.84. A sample for elemental analysis was prepared by heating a mixture of **6** and 7 at 80 °C for 2 h under high vacuum. Anal. Calcd for  $C_{73}H_{88}Al_4N_8$ : C, 73.96; H, 7.48; N, 9.45. Found: C, 72.90; H, 7.51; N, 9.49. The mother liquor gave another crop of crystals, which were found to be a mixture of **6**, 7, and **10**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) data for **10**: only Al–Me resonances are clear. The other ones are largely masked by the resonances of **6** and 7: -2.48, -2.28, -2.27, -0.70, -0.37, and -0.17 (six singlets of equal intensity, AlMe).

N-Phenylacetamidine with AlMe<sub>3</sub>. N-Phenylacetamidine (0.50 g, 3.73 mmol), AlMe<sub>3</sub> (1.86 mL, 2 M in toluene, 3.72 mmol), and hexane (15 mL). The filtrate afforded a mixture of 8 and 9 in 4:1 ratio (0.48 g, 73%) as colorless crystals after 5 days. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): the intensity of peaks for 8 and 9 are in 4:1 ratio.  $\delta$  –1.42 (s, 3H, AlMe (9)), -1.35 (s, 3H, AlMe (8)), -1.30 (s, 3H, AlMe (8)), -1.26 (s, 3H, AlMe (9)), -1.22 (s, 3H, AlMe (9)), -1.07 (s, 3H, AlMe (8)), -0.80 (s, 3H, AlMe (9)), -0.78 (s, 3H, AlMe (8)), -0.68 (s, 3H, AlMe (9)), -0.66 (s, 3H, AlMe (8)), 1.39 (s, 3H, CH<sub>3</sub> (8)), 1.83 (s, 3H, CH<sub>3</sub> (9)), 1.88 (s, 3H, CH<sub>3</sub> (8)), 1.88 (s, 3H, CH<sub>3</sub> (9)), 1.89 (s, 3H, CH<sub>3</sub> (9)), 1.90 (s, 3H, CH<sub>3</sub> (8)), 1.91 (s, 3H, CH<sub>3</sub> (8)), 1.96 (s, 3H, CH<sub>3</sub> (9)), 5.05 (s, 1H, NH (8)), 5.21 (s, 1H, NH (9)), 6.42 (m, br, 2H, ArH (8)), 7.00 - 7.35 (set of multiplets, 18H, ArH (8) and 20H, ArH (9)). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  -9.05, -8.75, -7.68, -6.95, 21.61, 24.34, 24.55, 25.28, 24.41, 25.44, 25.46, 25.83, 25.94, 26.25, 125.09, 125.40, 125.46, 125.67, 125.77, 126.51, 126.64, 127.71, 127.81, 128.04, 128.33, 128.38, 128.49, 128.66, 128.74, 128.94, 129.19, 129.28, 129.36, 129.46, 138.03, 144.99, 145.73, 147.07, 147.30, 147.35, 147.89, 174.15, 174.75, 175.19, 175.69, 176.31, 179.62, 180.00. Sample for elemental analysis was prepared by heating a mixture of 8 and 9 at 80 °C for 2 h under high vacuum. Anal. Calcd for C37H48Al4N8: C, 62.35; H, 6.79; N, 15.72. Found: C, 62.26; H, 6.81; N. 15.78.

N-Phenylbenzamidine with AlMe<sub>3</sub> (1:1.2 Ratio). N-Phenylbenzamidine (0.26 g, 1.33 mmol), AlMe<sub>3</sub> (0.80 mL, 2 M in toluene, 1.60 mmol), toluene (15 mL). Large blocks of colorless crystals of 11.2C7H8 (0.19 g, 57%) were obtained after 1 day at rt. After drying under vacuum, 11·2C7H8 lost a molecule of toluene. mp: 306-308 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  –3.02 (s, 3H, AlMe), –2.07 (s, 3H, AlMe), -1.77 (s, 3H, AlMe), -1.18 (s, 3H, AlMe), -0.62 (s, 3H, AlMe), -0.37 (s, 3H, AlMe), 0.11 (s, 3H, AlMe), 0.73 (s, 3H, AlMe), 2.36 (s, 3H, CH<sub>3</sub> (tol.)), 4.66 (m, 1H, ArH), 5.24 (m, 1H, ArH), 6.19 (m, 1H, ArH), 6.43 (m, 2H, ArH), 6.53 (m, 1H, ArH), 6.78-7.44 (set of multiplets, 46H, ArH), 7.53 (m, 1H, ArH), 7.65 (m, 1H, ArH), 7.98 (m, 1H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  –12.91, –9.21, –8.82, -8.17, -6.51, -5.57, -3.76, 21.61, 124.15, 124.23, 124.45, 124.66, 125.46, 125.79, 125.91, 126.27, 126.57, 127.02, 127.11, 127.19, 127.25, 127.44, 127.52, 127.59, 127.87, 127.92, 128.15, 128.19, 128.32, 128.38, 128.64, 128.66, 128.78, 128.79, 128.85, 128.94, 129.02, 129.19, 129.82, 129.96, 130.87, 131.76, 135.28, 138.03, 138.98, 139.19, 139.70, 141.07, 144.08, 144.94, 145.84, 147.06, 147.92, 176.97, 177.05, 179.77, 180.86, 185.25. Anal. Calcd for  $C_{80}H_{82}Al_6N_{10}\!\!:$  C, 71.41; H, 6.14; N, 10.41. Found: C, 71.48; H, 6.18; N, 10.35.

General Procedure for the Reaction of Amidines with AlMeCl<sub>2</sub>. To a solution of amidine (1 equiv) in a minimum amount of toluene, AlMeCl<sub>2</sub> (1 equiv) was added dropwise at room temperature and stirred for 15 min. All the volatiles were removed under vacuum, and the residue was heated to 170 °C for 2 h. The reaction mixture was cooled to room temperature, dissolved in toluene or a toluene–hexane mixture, and filtered using Celite.

**N-(Dipp)acetamidine with AlMeCl<sub>2</sub>.** *N*-(Dipp)acetamidine (0.48 g, 2.20 mmol), AlMeCl<sub>2</sub> (2.20 mL, 1 M in hexanes, 2.20 mmol), toluene (15 mL). The filtrate afforded X-ray quality crystals of  $12 \cdot C_7H_8$  (0.29 g, 41%). mp: 168–170 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.21 (m, 48H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.98 (s, 6H, CH<sub>3</sub>), 2.35 (s, 3H, toluene CH<sub>3</sub>), 2.86 (m, 10H, CH<sub>3</sub> and CH(CH<sub>3</sub>)<sub>2</sub>), 3.01 (m, 4H,

CH(CH<sub>3</sub>)<sub>2</sub>), 5.32 (s, 2H, NH), 7.12–7.40 (set of multiplets, 17H, ArH), 8.84 (s, 2H, NH), 10.73 (s, 2H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 17.86, 21.60, 22.34, 23.51, 23.73, 23.84, 24.45, 25.09, 28.95, 28.98, 124.25, 124.30, 125.44, 128.37, 129.18, 129.54, 130.01, 130.68, 133.47, 138.01, 145.88, 173.48, 174.62. Anal. Calcd for C<sub>63</sub>H<sub>86</sub>Al<sub>3</sub>Cl<sub>7</sub>N<sub>8</sub>: C, 58.91; H, 6.75; N, 8.72. Found: C, 58.78; H, 6.83; N, 8.65.

N-(Dipp)benzamidine with AlMeCl<sub>2</sub>. N-(Dipp)benzamidine (0.29 g, 1.04 mmol), AlMeCl<sub>2</sub> (1.00 mL, 1 M in hexanes, 1.00 mmol), toluene (15 mL), hexane (2 mL). The filtrate afforded X-ray quality crystals of 13.2C7H8 (0.12 g, 32%). Characterization data for 13·2C<sub>7</sub>H<sub>8</sub>: mp: 237 °C (dec). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.20 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.91 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.00 (m, 9H,  $CH(CH_3)_2$ , 1.20 (d, 3H,  $CH(CH_3)_2$ ), 1.25 (d, 3H,  $CH(CH_3)_2$ ), 1.31 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.46 (d, 3H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.50 (d, 9H, CH(CH<sub>3</sub>)<sub>2</sub>), 2.36 (s, 6H, CH<sub>3</sub> (tol.)), 2.78 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.05 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.39 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.50 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 3.63 (s, 1H, NH), 3.80 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.77 (m, 1H, ArH), 6.84 (m, 2H, ArH), 6.95 (m, 5H, ArH), 7.11-7.30 (set of multiplets, 26H, ArH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.53, 21.61, 22.53, 22.89, 24.19, 24.45, 24.96, 25.24, 25.62, 26.09, 26.19, 27.27, 27.87, 28.44, 28.80, 29.16, 123.44, 123.86, 123.91, 124.32, 124.36, 124.47, 125.46, 126.62, 127.80, 127.85, 128.11, 128.39, 129.20, 129.71, 130.13, 131.00, 131.14, 131.30, 133.95, 136.21, 136.87, 137.44, 138.03, 138.53, 144.25, 144.61, 145.33, 145.57, 145.92, 146.05, 173.47, 175.14, 185.95. Anal. Calcd for C71H84Al3Cl5N6: C, 66.64; H, 6.62; N, 6.57. Found: C, 66.54; H, 6.59; N, 6.50. The mother liquor gave a further crop of colorless crystals, which were found to be of 14 (0.18 g, 43%). Characterization data for 14. mp: 178-179 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ): two sets of peaks in a 1:3 ratio were observed.  $\delta$  1.01 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub> minor), 1.22 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub> minor), 1.26 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub> major), 1.35 (d, 6H, CH(CH<sub>3</sub>)<sub>2</sub> major), 3.02 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub> major), 3.10 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub> minor), 5.80 (s, 1H, NH, major), 6.05 (s, 1H, NH minor), 7.12 (m, 2H, ArH minor), 7.35 (set of multiplets, 3H, ArH, NH major and 5H, ArH minor), 7.50 (m, 1H, ArH minor), 7.56 (m, 1H, ArH major), 7.65 (m, 2H, ArH major), 7.74 (m, 1H, ArH major), 7.91 (m, 2H, ArH major), 8.80 (s, 1H, NH minor). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 21.91, 23.49, 24.41, 25.36, 28.96, 29.20, 124.40, 125.61, 126.15, 128.07, 128.32, 129.19, 129.83, 130.12, 130.66, 131.86, 133.97, 145.32, 146.82, 170.90, 171.08. Anal. Calcd for C<sub>19</sub>H<sub>24</sub>AlCl<sub>3</sub>N<sub>2</sub>: C, 55.16; H, 5.85; N, 6.77. Found: C, 55.10; H, 5.90; N, 6.70.

**N-Phenylbenzamidine with AlMeCl<sub>2</sub>.** *N*-Phenylbenzamidine (0.32 g, 1.63 mmol), AlMeCl<sub>2</sub> (1.60 mL, 1 M in hexanes, 1.60 mmol), toluene (15 mL). The filtrate afforded colorless, X-ray quality crystals of **15** (0.29 g, 55%). mp: 199–200 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.05 (s, 1H, NH), 6.46 (s, 0.7H, NH), 6.91 (m, 2H, ArH), 7.24 (m, 2H, ArH), 7.40 (m, 6H, ArH), 7.54 (m, 2H, ArH), 7.62 (m, 4H, ArH), 7.73 (m, 1H, ArH), 7.91 (m, 2H, ArH), 9.32 (s, 1H, NH). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 124.96, 125.54, 127.88, 128.45, 128.63, 129.61, 129.79, 130.24, 131.39, 133.35, 134.19. Anal. Calcd for  $C_{13}H_{12}AlCl_3N_2$ : *C*, 47.37; H, 3.67; N, 8.50. Found: C, 47.17; H, 3.77; N, 8.45.

**N-(Dipp)benzamidine-AlCl<sub>3</sub> Adduct with AlMe<sub>3</sub>.** AlMe<sub>3</sub> (0.24 mL, 2 M in toluene, 0.48 mmol) was added dropwise to a solution of N-(Dipp)benzamidine-AlCl<sub>3</sub> adduct (0.20 g, 0.48 mmol) in toluene (2 mL) at room temperature and stirred for 15 min. All the volatiles were removed under vacuum, and the residue was heated to 170 °C for 2 h. The reaction mixture was cooled to room temperature, dissolved in a mixture of 15 mL of toluene and 3 mL of hexane, and filtered. The filtrate afforded colorless crystals of **13** (0.08 g, 44%) overnight.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Crystallographic information files (CIF) for 3, 4, 6, 8, and 10– 15; ORTEP diagrams and crystal data of 6, 8, and 15; and <sup>1</sup>H NMR spectra of 6, 7, and 10 (Al–Me region). This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### Corresponding Author

\*E-mail: ndreddy.che@pondiuni.edu.in.

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#### DEDICATION

Dedicated to Prof. Anil K. Bhatnagar on the occasion of his 70th birthday.

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