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Reactions of an Aluminum Amide with Aromatic Nitriles: Formation of Al−N−C Frameworks[†]

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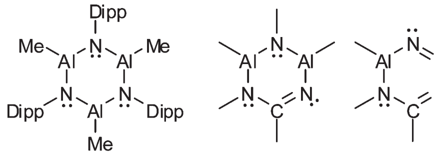
Reactions of a four-membered Al−N ring, [(Dipp)HNAlMe$_2$]$_2$ (**2**; Dipp = 2,6-diisopropylphenyl), with the aromatic nitriles PhCN, TbpCN (Tbp = 4-*tert*-butylphenyl), DmpCN (Dmp = 2,6-dimethylphenyl), DepCN (DepCN = 2,6-diethylphenyl), and DippCN are reported. **2** reacts with PhCN to give a 1:2 insertion product, the tetrameric aluminum amidinate **3**, whereas with TbpCN it gives the 1:1 insertion products **4**−**6**. Under similar conditions, DmpCN, DepCN, and DippCN do not undergo insertion but form simple adducts of alumazene (**1**), **7a**−**c** and **8a**−**c** (2:1 and 1:1 nitrile/alumazene), in which the nitriles coordinate to Al. Compounds **3**−**6** and **7a**−**c** have been structurally characterized. **3** is comprised of four four-membered aluminum amidinate rings. **5** features a core made of three Al$_2$N$_2$ and two AlCN$_2$ four-membered rings fused together. The structures of **4** and **6** consist of a dimer of a six-membered Al$_2$CN$_3$ framework. A high-yield synthesis of **3** from *N*-(Dipp)benzamidine and AlMe$_3$ has also been reported.

Introduction

The functional group C≡N (as in nitriles and the dicyanamide anion) has been extensively employed in the synthesis of carbon-containing inorganic heterocycles.[1] Reactions of alanes with nitriles and isonitriles have been well documented,[2] and these hydroalumination reactions lead to the formation of simple Al−N heterocycles, in the case of bulky alanes,[3] or three-dimensional Al−N networks, in the case of simple alanes.[4] Recently, there has been increased interest in the synthesis of Al−N and Al−C heterocycles/clusters from hydrazines and alkynes.[5] The strategy of inserting C−N multiple bonds into M−N or M−C (M = Li, Al)[6] bonds has been utilized in the synthesis of the corresponding metallacycles. While the insertion of nitriles into Al−N bonds was reported as early as 1969,[7] and the method was used for the synthesis of amidines in 1990,[8] so far there have been no reports on the structural characterization of aluminum amidinates involved in those reactions.



Alumazene, **1**

Carbaalumazenes

Figure 1

Although borazine has been known since 1926, its heavier congener, alumazene, was not known until 1988.[9] The

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[†] Dedicated to Prof. Dr. h.c. mult. Herbert W. Roesky on the occasion of his 75th birthday.

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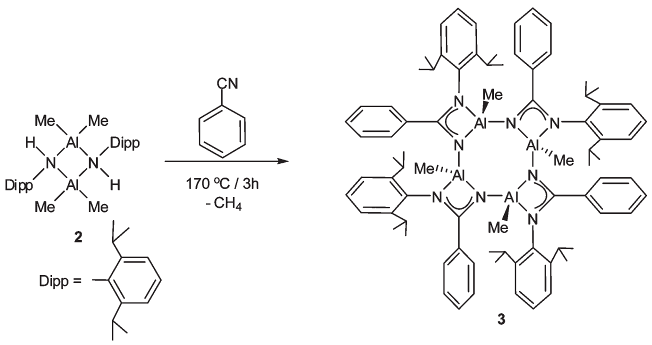
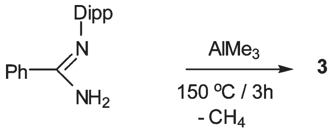
difficulty in synthesizing Al–N heterocycles, containing three-coordinated Al and N atoms, arises from the tendency of both Al and N to form four-coordinated species. The only known example of alumazene, $(MeAlNDipp)_3$ (**1**; Dipp = 2,6-diisopropylphenyl), was prepared by a two-stage methane elimination reaction between $AlMe_3$ and a bulky amine, $DippNH_2$. Replacing one or two Al atoms from the skeletal framework of **1** by C leads to a new class of heterocycles, carbaalumazenes (Figure 1), structurally similar to carbaphosphazenes[10] and carbathiazenes,[11] which have attracted much attention because of their applications. The boron analogue of such heterocycles, a six-membered carbaborazine (triazadiboracyclohexane), has been synthesized from a reaction between 2 equiv of an iminoborane and 1 equiv of ^iPrCN.[1d] In this context, we explored the reactions of the sterically encumbered aluminum amide **2** with some aromatic nitriles and the results are reported herein.

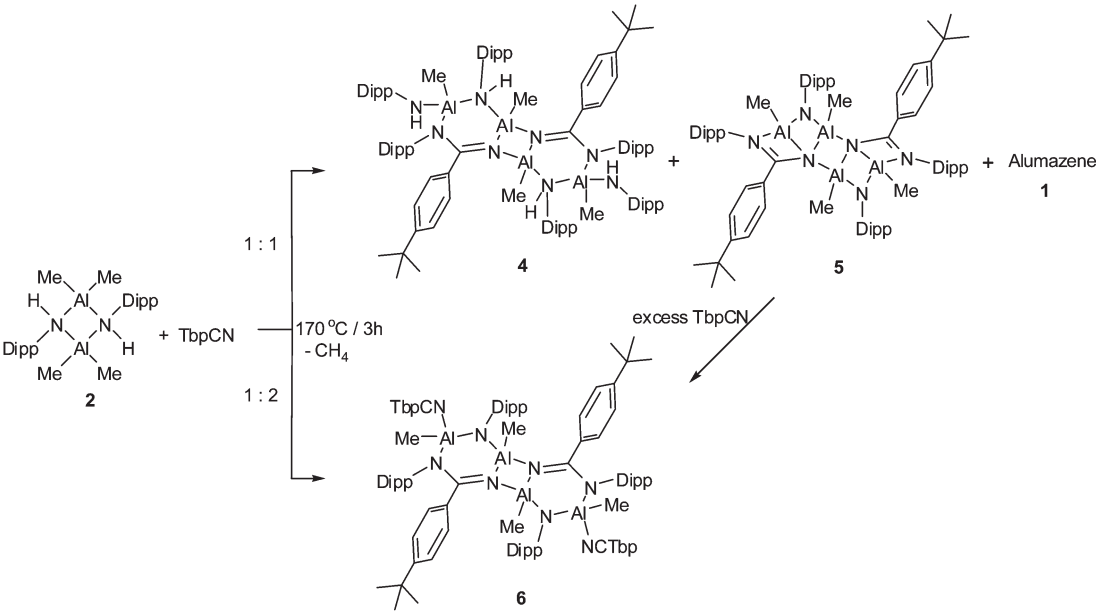
Scheme 1. Reaction of Aluminum Amide with Benzonitrile



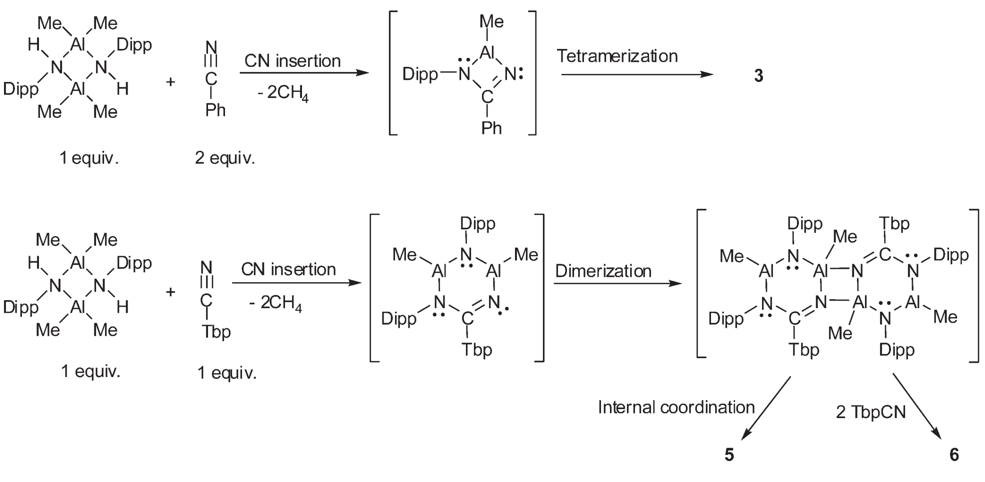
Scheme 4. Synthesis of 3 from *N*-(Dipp)benzamidine



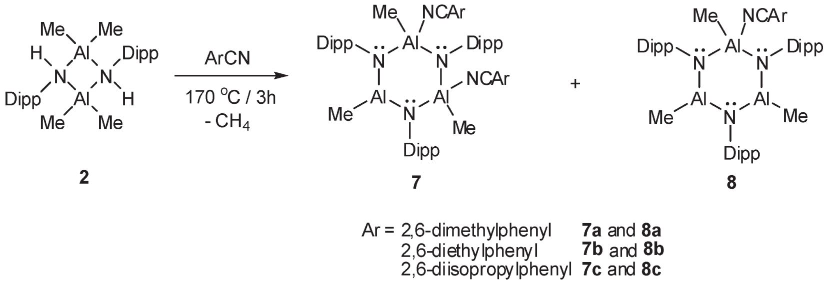
Scheme 2. Reactions of Aluminum Amide with 4-*tert*-Butylbenzonitrile



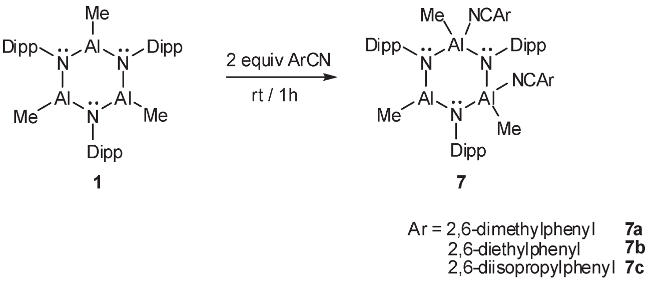
Scheme 3. Plausible Transformations Involved in the Formation of 3, 5, and 6



Scheme 5. Reactions of Aluminum Amide with 2,6-Dialkylbenzonitriles



Scheme 6. Reactions of Alumazene (1) with 2,6-Dialkylbenzonitriles



Results and Discussion

Reactions of the aluminum amide **2** with aromatic nitriles were carried out at 170 °C in 1:1 and 1:2 molar ratios. In all these reactions, evolution of methane was observed around 100 °C and the resultant residue was recrystallized from hexanes. A 1:1 or 1:2 molar mixture of **2** and PhCN afforded the tetrameric aluminum amidinate **3** in low yields (Scheme 1). **3**, which is an insertion product of two molecules of PhCN per molecule of **2**, is the only isolated product from both 1:1 and 1:2 reactions.

A thorough ^{1}H NMR analysis of the mother liquor showed a mixture of Al compounds (based on Al–Me and ^{i}Pr resonances), including **3**, and our attempts to isolate any further pure compounds from this mixture were unsuccessful. Pentane, presumably from hexanes, was present in the crystal lattice and could not be removed even after drying the crystals under high vacuum for several hours.

Interestingly, in the case of TbpCN, the three products **4** and **5** (from a 1:1 molar ratio) and **6** (from a 1:2 molar ratio) were obtained, depending on the stoichiometry of **2** and the nitrile (Scheme 2). All the compounds are formed due to insertion of one CN (CN = nitrile functional group) per molecule of **2**. The second molecule of TbpCN, in the case of a 1:2 (**2**/nitrile) mixture, does not undergo insertion but simply coordinates to one of the Al atoms, giving **6**. Slow evaporation of a hexane solution of the residue obtained from the 1:1 reaction initially afforded colorless crystals of **4** in very low yield. Further evaporation of the mother liquor yielded a good amount of yellow crystals, which were later identified as **5**. Sublimation of the final residue gave some amount of **1**. Compound **5** is the major product among the isolated species. In the case of a 1:2 (**2**/nitrile) reaction, colorless, rhombic-prismatic crystals of **6** were obtained by storing a solution of the reaction mixture either in hexanes or in toluene overnight at room temperature. No further compounds were isolated from the mother liquor, either by crystallization or by sublimation. Compound **6** is highly insoluble in common hydrocarbon solvents, and therefore no NMR could be obtained. **6** can readily be prepared by the addition of excess of TbpCN to **5** in quantitative yield. When a solution of **5** in hexanes was treated with TbpCN, colorless crystals of **6** were formed overnight. The formation of **6** in this reaction was confirmed by comparing single-crystal X-ray structural data. ^{1}H NMR spectra of **4** and **5** agree well with their solid-state structures, but resonances related to some of the ^{i}Pr groups in **5** are broad.

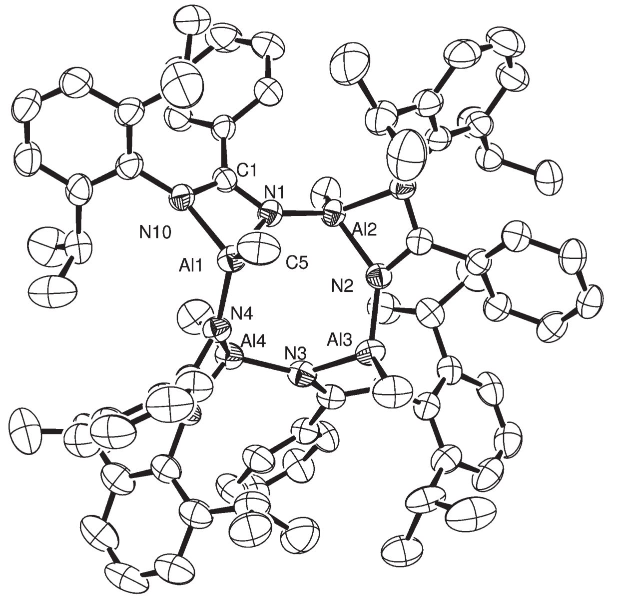


Figure 2. Single-crystal X-ray structure of **3**. Pentane and hydrogen atoms are not shown for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Al1–N1 = 1.914(7), Al1–N10 = 1.937(7), Al1–C5 = 1.938(9), N1–C1 = 1.333(10), N10–C1 = 1.330(10), Al1–N4 = 1.827(7), Al4–N4 = 1.916(7), Al4–N3 = 1.821(7), Al3–N3 = 1.899(7), Al3–N2 = 1.823(7), Al2–N2 = 1.897(7), Al2–N1 = 1.826(7). Selected bond angles (deg): N4–Al1–N1 = 109.1(3), Al1–N1–Al2 = 140.9(4), N4–Al1–C5 = 122.5(4), N1–C1–N10 = 113.3(7), N1–Al1–N10 = 70.6(3), Al1–N1–C1 = 88.4(5).

As illustrated in Scheme 3, formation of compounds **3**, **5**, and **6** can be explained in terms of (1) elimination of methane and (2) insertion of CN into Al–N bonds, followed by (3) oligomerization of intermediates and further coordination. Either simultaneous or stepwise occurrence of the first two

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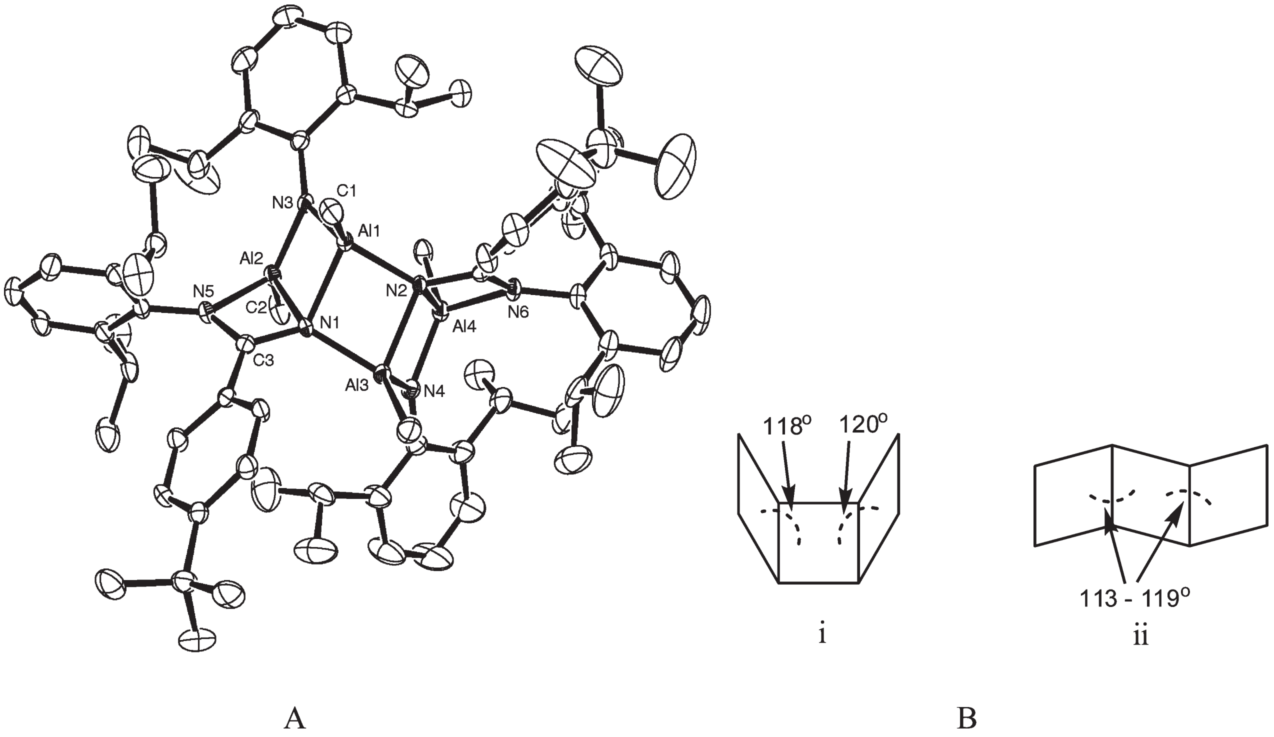

Figure 3. (A) Single-crystal X-ray structure of **5**. Hexane and hydrogen atoms are not shown for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Al1−N1 = 2.0113(19), Al3−N2 = 2.0133(19), Al1−N2 = 1.918(2), Al3−N1 = 1.910(2), Al1−N3 = 1.831(2), Al3−N4 = 1.833(2), Al2−N3 = 1.809(2), Al4−N4 = 1.804(2), Al2−N5 = 1.940(2), Al4−N6 = 1.941(2), Al2−N1 = 2.023(2), Al4−N2 = 2.038(2), Al1−C1 = 1.953(3), C3−N5 = 1.323(3), C3−N1 = 1.367(3). Selected bond angles (deg): Al1−N1−Al3 = 94.43(8), N1−Al1−N2 = 83.61(9), Al1−N1−Al2 = 83.12(8), Al1−N3−Al2 = 94.66(10), N1−C3−N5 = 112.9(2), N1−Al2−N5 = 68.89(8), Al2−N1−Al3 = 125.33(10), N3−Al1−N2 = 113.08(10), N5−Al2−C2 = 112.86(10), N1−Al2−C2 = 116.76(11), N3−Al2−C2 = 129.83(10). (B) Three fused four-membered Al_2N_2 rings found (i) in **5** and (ii) in compounds reported in refs 15a−15d. Angles between the mean planes of the rings are shown.

processes presumably results in intermediates containing two coordinated N and three coordinated Al atoms; hence, they have enough room to associate themselves into interesting structures. In the case of TbpCN, three-coordinated Al atoms, present in the dimerized product, are further coordinated either by internal N atoms to form **5** or by additional TbpCN molecules to form **6**. The presence of only one Me group on each Al atom and the absence of N−H units in these compounds suggest the elimination of methane, which was confirmed by trapping it from a reaction between **2** and PhCN.

After **3** was fully characterized, it was felt that it could be synthesized from an appropriate benzamidine. *N*-(Dipp)benzamidine was prepared from PhCN and $DippNH_2$ and subsequently treated with $AlMe_3$ at 150 °C for 3 h. The resultant crystalline substance was recrystallized from toluene to give colorless crystals of **3** in 88% yield (Scheme 4). There are several examples of a reaction between $AlMe_3$ and N,N′-disubstituted amidines known in the literature.[6b,12] However, to the best of our knowledge, there have been no reactions of $AlMe_3$ with N-monosubstituted amidines reported so far.

Reactions of **2** with the sterically demanding 2,6-dialkylbenzonitriles DmpCN, DepCN, and DippCN are straightforward and simple. No CN insertion products were isolated in any of these reactions. This can be attributed to the steric encumbrance caused by the alkyl groups present in ortho positions of the benzonitrile in addition to having large Dipp substitutions on the amido N of **2**. Under the reaction conditions, **2** underwent thermolysis to give **1** and the nitriles coordinated to Al atoms, forming 1:2 and 1:1 adducts (**7** and **8**, Scheme 5).

Surprisingly, ^1H NMR spectra of the isolated 1:2 adducts **7a**−**c** at room temperature were simple and do not correlate with the solid-state structures. For example, **7c** is expected to show two resonances for Al−Me protons and two for methine protons of **1**, but the spectrum shows only one resonance for each type, typical of **1** (D_{3h}). The whole spectrum looks like that of a simple 1:2 mixture of **1** and DippCN with a slight upfield shift of ^{i}Pr CH protons (about 0.3 ppm) of DippCN and a downfield shift of ^{i}Pr CH protons (about 0.8 ppm) and Al−Me protons (about 0.2 ppm) of **1**. However, upon cooling, all the peaks related to **1** became broad and at −30 °C the Al−Me peak splits into two (1:2 ratio) while the ^{i}Pr CH peak divides into three broad peaks. Similar behavior was also observed in the cases of **7a**,**b**. From these observations we infer that these adducts exhibit a dynamic interaction between **1** and the nitriles in solution at room temperature. However, other evidence for this dynamic behavior came from NMR tube experiments carried out between **1** (independently prepared) and DippCN in 1:1, 1:2, and 1:3 molar ratios. All of them showed the same number of resonances with the same chemical shifts as observed for **7c**, but with appropriate integral ratios.

In all the cases, the mother liquor shows a ^1H NMR spectrum similar to that of **7** but with different integral ratios

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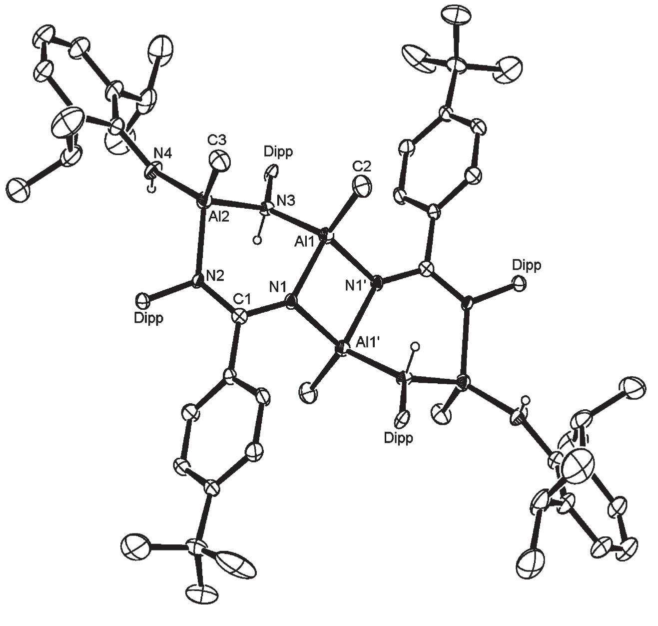

Figure 4. Single-crystal X-ray structure of **4**. Dipp groups on skeletal N are represented by ipso carbon atoms, and hydrogen atoms (except on N) are not shown for clarity. Thermal ellipsoids are drawn at the probability level. Al1−N1 = 1.881(2), Al1−N1′ = 1.894(2), N1−C1 = 1.338(3), N2−C1 = 1.348(3), N2−Al2 = 1.957(2), Al2−N3 = 1.998(2), Al1−N3 = 1.954(2), Al2−N4 = 1.814(2), Al2−C3 = 1.947(3), Al1−C2 = 1.944(3). Selected bond angles (deg): N1−Al1−N1′ = 86.32(9), Al1−N1−Al1′ = 93.68(9), N1−Al1−N3 = 94.63(10), N1−C1−N2 = 122.9(2), C1−N2−Al2 = 125.38(18), N2−Al2−N3 = 95.85(9), Al1−N3−Al2 = 106.24(11), N2−Al2−N4 = 117.06(11), N3−Al2−N4 = 104.42(11), N4−Al2−C3 = 116.66(13), N2−Al2−C3 = 106.48(12), N3−Al2−C3 = 114.72(12).

of **1** to nitrile resonances, which can be interpreted for a mixture of **7** and **8**. Alternatively, **7a**−**c** were synthesized as crystalline solids in good yields from the reaction between **1** and the appropriate 2,6-dialkylbenzonitriles in toluene (Scheme 6). In a typical reaction, the mixture was stirred in toluene for 1 h at room temperature, the solvent was evaporated, and the residue was dissolved in the minimum amount of hexanes. Colorless crystals of **7a**−**c** were obtained in a few minutes. Alumazene (**1**) is highly reactive compared to its boron analogue, and quite a few reactions of **1** have been reported in the literature.[13]

Compounds **3**−**6** and **7a**−**c** have been structurally characterized, and their ORTEP diagrams are given in Figures 2−8, respectively. Bond lengths and bond angles for compounds **3**−**6** are provided in the captions to Figures 2−5, and those for compounds **7a**−**c** are given in Table 1. The basic structure of **3** can be constructed by connecting four four-membered aluminum amidinate rings through imido N (N1, N2, N3, and N4) and Al on each ring. The eight-membered ring, comprised of alternating Al and N atoms, is in a boat conformation with

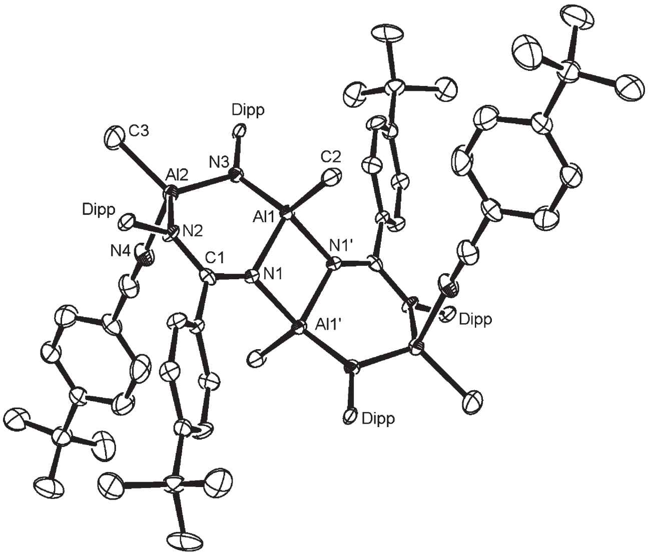

Figure 5. Single-crystal X-ray structure of **6**. Dipp groups are represented by ipso carbon atoms, and toluene molecules and hydrogen atoms are not shown for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Al1−N1 = 1.918(3), Al1−N1′ = 1.895(2), N1−C1 = 1.306(4), N2−C1 = 1.373(3), N2−Al2 = 1.892(2), Al2−N3 = 1.808(3), N3−Al1 = 1.825(2), Al2−N4 = 2.009(3), Al2−C3 = 1.944(3), Al1−C2 = 1.971(3). Selected bond angles (deg): N1−Al1−N1′ = 86.67(11), Al1−N1−Al1′ = 93.33(11), N1−Al1−N3 = 105.23(11), N1−C1−N2 = 118.7(3), C1−N2−Al2 = 118.6(2), N2−Al2−N3 = 114.36(11), N4−Al2−N2 = 97.53(11), N4−Al2−C3 = 104.73(13), N4−Al2−N3 = 107.77(12), C3−Al2−N3 = 117.79(13), C3−Al2−N2 = 111.99(13), Al1−N3−Al2 = 109.44(13).

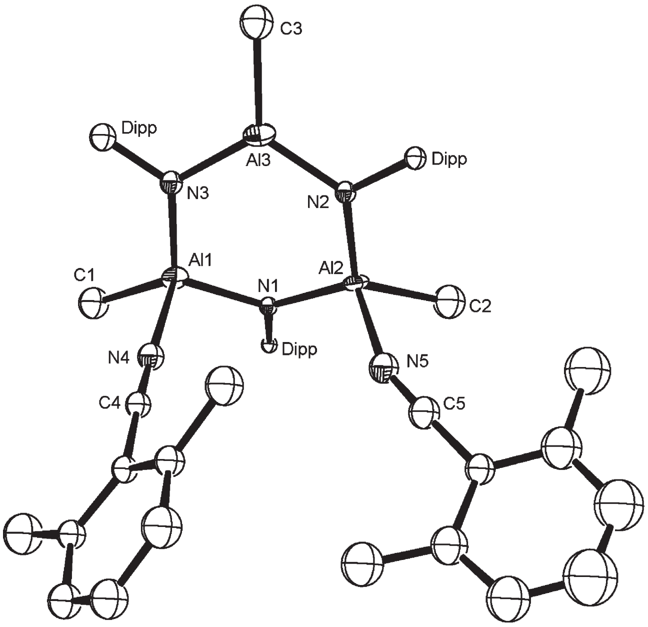

Figure 6. Single-crystal X-ray structure of **7a**. Another independent molecule from the asymmetric unit and hydrogen atoms are eliminated for clarity. Dipp groups of alumazene are represented by ipso carbons. Thermal ellipsoids are drawn at the 50% probability level.

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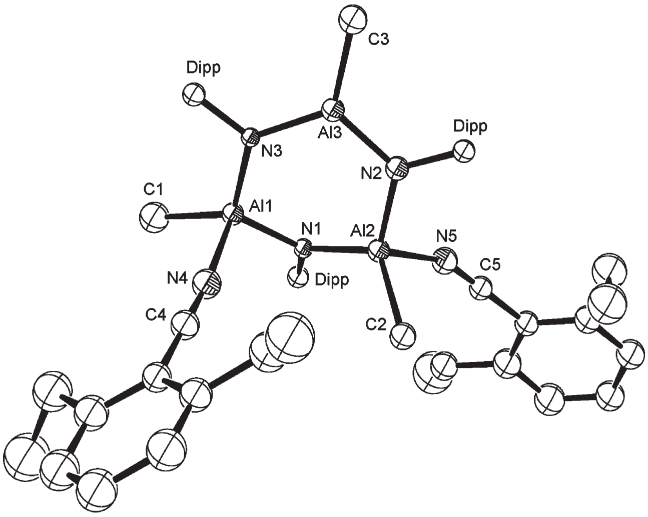

Figure 7. Single-crystal X-ray structure of **7b**. Only one of fthe our independent molecules from the asymmetric unit is shown. Dipp groups are represented by ipso carbons. Hydrogen atoms are eliminated for clarity. Thermal ellipsoids are drawn at the 50% probability level.

methyl groups on the Al atoms projecting out on either side of the ring. While all the N atoms are three-coordinated in a planar geometry, all the Al atoms are four-coordinated in a distorted-tetrahedral geometry. Despite the fact that the coordination numbers for Al and N are constant throughout the molecule, there is a variation in Al−N bond length. The shortest is that which is exocylic to the amidinate ring (average 1.824 Å). The longest is between Al and the Dipp-substituted N (average 1.931 Å). Bond angles and bond lengths within the amidinate ring are in agreement with those reported in the literature.[6b,c,12c,14] An interesting feature of this molecule is the fact that the bridging amidinate N atoms are three-coordinate and no such compounds have been reported so far. The ^{1}H and ^{13}C NMR spectra of **3** (C_6D_6 or $CDCl_3$) support the position that the solid-state structure is retained in solution.

5 crystallizes in the space group $P2_1/n$ with a molecule of hexane. It consists of three fused four-membered Al_2N_2 rings. There is a four-membered amidinate ring fused to each terminal Al_2N_2 ring sideways (Figure 3). There are five structures with three fused Al_2N_2 rings reported in the literature.[15] All of them contain the rings fused in a chair conformation ("Z" shaped), but in **5** they adopt a boat conformation ("U" shaped). The angles between the mean planes of the rings have been compared with those reported, and they are found to be in a similar range except for one structure[15e] (143°). The central Al_2N_2 ring is slightly puckered, while the terminal rings are planar but rhomboid. As with the previously reported structures, different Al−N bonds were found. The shortest bond (Al4−N4 = 1.804(2) Å) is between three-coordinated N and four-coordinated Al. The longest one (Al3−N2 = 2.0133(19) Å) is between the four-coordinated atoms.

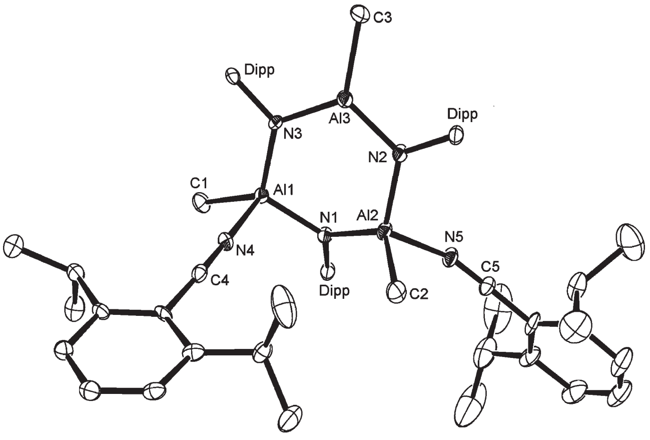

Figure 8. Single-crystal X-ray structure of **7c**. Another independent molecule from the asymmetric unit and hydrogen atoms are eliminated for clarity. Dipp groups of alumazene are represented by ipso carbon atoms. Thermal ellipsoids are drawn at the 50% probability level.

The basic structures of centrosymmetric molecules **4** and **6** (Figures 4 and 5) are closely similar, and both contain a dimer of the Al_2CN_3 ring coordinated externally by two DippNH units (in **4**) or two TbpCN molecules (in **6**). Six-membered rings in **4** are highly puckered compared to those in **5**. While DippNH-coordinated Al atoms are in a distorted-tetrahedral geometry, TbpCN-coordinated Al atoms are in a trigonal-pyramidal geometry. Variation in Al−N bond lengths is found in both molecules. The externally coordinated amido nitrogen forms the shortest Al−N bond (Al2−N4 = 1.814(2) Å) in **4**, whereas the bond between nitrilic nitrogen and Al is the longest in **5** (Al2−N4 = 2.009(3) Å). There is also a variation in ring C−N bonds. Though the variation is small compared to that of the Al−N bond, it is more pronounced in **6** than in **4**. In **6**, the bond between C and imido N (C1−N1 1.306(4) Å) is shorter than that between C and the Dipp-substituted N (C1−N2 = 1.373(3) Å). The four-membered Al_2N_2 rings in both structures are planar and slightly rhomboid. All the ring N and C atoms in **6** are in a plane with their neighboring atoms. The sum of bond angles around these atoms is equal to 360°.

The molecular structures of **7a**−**c** feature a puckered Al_3N_3 ring in which two of the Al atoms are coordinated by nitriles. In **7a**, both DmpCN molecules occupy axial positions in a cis fashion. However, in **7b**,**c**, the nitriles are arranged in a trans geometry with one nitrile in an axial position and the other in an equatorial position. Similar adducts of **1** with pyridine have been reported in the literature.[13a] In the same article, formation of weak cis and trans adducts of nitriles with **1** was cited as unpublished results. In all the cases (**7a**−**c**), one of the two C≡N−Al bond angles (equatorial in the case of trans adducts) deviates from linearity by 25−30°. All bond angles and bond lengths in the six-membered Al_3N_3 ring are within the range of those reported in ref 13a.

Conclusion

The present study was aimed at synthesizing six-membered carbaalumazenes by inserting CN into Al−N bonds. When sterically nondemanding nitriles such as PhCN and TbpCN

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Table 1. Selected Bond Lengths and Bond Angles for Compounds 7a−c

	7a	7b	7c		7a	7b	7c
			Bond Lengths (Å)				
Al1−N1	1.822(5)	1.812(5)	1.810(4)	Al2−N1	1.791(6)	1.808(5)	1.811(4)
Al1−N3	1.820(6)	1.841(5)	1.830(4)	Al2−N5	2.063(7)	2.012(6)	2.003(5)
Al1−N4	2.058(6)	2.032(6)	2.030(4)	Al1−C1	1.967(7)	1.958(6)	1.945(5)
Al3−N3	1.806(6)	1.787(5)	1.771(4)	Al2−C2	1.973(6)	1.972(6)	1.973(5)
Al3−N2	1.777(6)	1.788(6)	1.765(4)	Al3−C3	1.959(7)	1.948(6)	1.949(5)
Al2−N2	1.820(6)	1.832(6)	1.838(4)				
			Bond Angles (deg)				
N1−Al1−N3	113.6(3)	112.2(2)	111.33(18)	Al1−N1−Al2	126.0(3)	119.7(2)	119.9(2)
C1−Al1−N4	99.8(3)	99.0(3)	97.80(19)	N2−Al2−N1	109.5(3)	111.4(3)	111.56(18)
N1−Al1−N4	103.0(3)	103.3(3)	101.85(17)	N1−Al2−N5	110.1(2)	106.7(2)	106.95(19)
N3−Al1−N4	101.0(2)	100.4(2)	103.28(17)	C2−Al2−N5	91.5(3)	94.1(3)	94.0(2)
Al3−N3−Al1	120.6(3)	122.9(3)	123.4(2)	N2−Al2−N5	101.9(3)	106.4(3)	105.71(18)
N3−Al3−N2	116.9(3)	117.0(3)	118.58(19)	Al1−N4−C4	177.0(6)	175.1(6)	169.7(4)
Al3−N2−Al2	126.6(3)	121.9(3)	120.4(2)	Al2−N5−C5	154.6(6)	155.8(6)	150.8(4)

were employed, CN insertion took place but dimers and tetramers were formed. These associations were anticipated on the basis of the fact that simple CN insertions would lead to the formation of fugitive species with two-coordinated N and three-coordinated Al. Nonetheless, compounds **3−6** offer unique and interesting structural motifs. On the other hand, no CN insertion was observed in the case of 2,6-dialkylbenzonitriles, where the CN group is sterically hindered by ortho substitutions. Formation of **3** in high yield in a reaction between *N*-(Dipp)benzamidine and $AlMe_3$ gives an insight into how an N-monosubstituted amidine reacts with $AlMe_3$.

Experimental Section

General Considerations. All manipulations were carried out under an N_2 atmosphere using a Schlenk line and a glovebox. Trimethylaluminum was procured from Aldrich Chemical Co. and used as received. 2,6-Diisopropylaniline (CaH_2), PhCN (from P_2O_5), and hexanes and toluene (from Na/benzophenone ketyl) were distilled fresh when required. Benzene-d_6 and toluene-d_8 were condensed from Na/benzophenone ketyl and stored in a glovebox. $[Me_2AlNH(Dipp)]_2$,[9] $[MeAlN(Dipp)]_3$,[9] 2,6-dialkylbenzonitriles,[16] and TbpCN[17] were prepared using literature procedures. ^1H and ^{13}C spectra were recorded on Bruker 500 or 400 MHz instruments. Elemental analyses were performed by the Analytisches Labor des Institut für Anorganische Chemie der Universität Göttingen.

Structural Determination for 3−6 and 7a−c. Crystals of **3** and **7a−c**, suitable for X-ray diffraction, were obtained by storing solutions of reaction mixtures in hexane at room temperature for 2 days, and those of **4** and **5** were grown by slow evaporation of a hexane solution of the reaction mixture. Rhombic-prismatic single crystals of **6** were obtained from toluene solution at room temperature. In order to avoid quality degradation, the single crystals (except **4**) were mounted on a glass fiber in perfluoropolyalkyl ether oil/paraffin oil and then brought into the cold nitrogen stream of a low-temperature device so that the oil solidified. A paraffin oil coated crystal of **4** was mounted on a glass fiber using epoxy glue, and the data were collected at room temperature. Data collection for **3** and **7c** was performed on a STOE STADI 4 diffractometer and for **4−6** and **7a**,**b** on an OXFORD XCALIBUR diffractometer, both equipped with a CCD area detector, using graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation and a low-temperature device. All calculations were performed using SHELXTL (version 6.12) or SHELXS-97 and SHELXL-97.[18] 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 in **3−6** and **7c** were refined anisotropically (except the pentane molecule in **3** and one toluene molecule in **6**). In **7a** only Al atoms were given anisotropic treatment. One DepCN moiety of **7b** was refined isotropically. 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 X-ray structures showed no significant peaks.

There are four molecules in the asymmetric unit of **7b**. One DepCN unit in one of these molecules is severely disordered and could not be modeled properly. All the other atoms in the cell were refined anisotropically. Three sets of data were collected using crystals from three different batches. All the data sets gave similar results. The asymmetric unit of structure **7c** contains two molecules, each showing somewhat larger displacement ellipsoids of some substituents on the aryl rings. Several attempts to solve the structure of **7c** in a centrosymmetric space group failed. All the data sets were collected to 2θ values > 50°. Relevant data concerning crystallographic data, data collection, and refinement details are summarized in Table 2. 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 781145−781151. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

Reaction of 2 with Nitriles. In a typical reaction, a mixture of **2** (1 equiv) and nitrile (1 or 2 equiv) was taken in a Schlenk flask and heated to 170 °C for 3 h. After the reaction mixture was cooled to room temperature, the residue was dissolved in hexanes and filtered using Celite.

With PhCN. **2** (3.00 g, 6.4 mmol), PhCN (0.66 g, 6.4 mmol), hexane (20 mL). The filtrate afforded X-ray-quality colorless crystals of $\mathbf{3}\cdot{}^1/_2C_5H_{12}$ (0.50 g, 12%). Mp: >300 °C dec. ^1H NMR (400 MHz, C_6D_6): δ −0.32 (s, 12H, AlMe), 1.74 (d, 12H, $CH(CH_3)_2$), 0.86 (m, 3H, pentane CH_3), 1.13 (d, 12H, $CH(CH_3)_2$), 1.23 (m, 15H, $CH(CH_3)_2$ and pentane CH_2), 1.40 (d,

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(17) TbpBr from *tert*-butylbenzene: (a) Furniss, B. S; Hannaford, A. J.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Pearson Education: Singapore, 1989; p 861. TbpCN from TbpBr: (b) Reference 16b.

(18) (a) *SHELXTL v6.12*; Bruker AXS Instruments Inc., Madison, WI,, 2000. (b) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

Table 2. Crystal Data for Complexes 3−6 and 7a−c

	3·$^1/_2C_5H_{12}$	**4**	**5**·C_6H_{14}	**6**·$4C_7H_8$	**7a**	**7b**	**7c**
empirical formula	$C_{82.5}H_{106}Al_4N_8$	$C_{98}H_{144}Al_4N_8$	$C_{80}H_{120}Al_4N_6$	$C_{124}H_{164}Al_4N_8$	$C_{57}H_{78}Al_3N_5$	$C_{61}H_{86}Al_3N_5$	$C_{65}H_{94}Al_3N_5$
formula wt	1317.67	1542.13	1273.74	1874.55	914.18	970.29	1026.39
temp (K)	200(2)	293(2)	150(2)	150(2)	150(2)	150(2)	200(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1$	$P\bar{1}$	$Pca2_1$
Flack param					−0.3(2)		0.43(15)
a (Å)	11.247(2)	15.7017(15)	16.9091(5)	13.6963(4)	12.2880(14)	12.2943(5)	25.157(5)
b (Å)	28.468(6)	17.1465(9)	18.1419(5)	17.2583(6)	20.243(3)	28.7826(11)	14.943(3)
c (Å)	25.068(5)	17.9144(13)	25.6946(8)	23.8216(9)	12.5337(16)	34.8658(14)	34.178(7)
α (deg)	90	90	90	90	90	97.869(3)	90
β (deg)	93.75(3)	105.631(9)	95.189(2)	95.751(3)	115.408(15)	95.239(3)	90
γ (deg)	90	90	90	90	90	101.317(3)	90
V (Å^3)	8009(3)	4644.7(6)	7849.9(4)	5602.5(3)	2816.2(7)	11894.8(8)	12848(4)
Z	4	2	4	2	2	8	8
ρ_{calcd} (Mg m^{-3})	1.093	1.103	1.078	1.111	1.078	1.084	1.061
μ (mm^{-1})	0.104	0.099	0.103	0.093	0.106	0.104	0.099
F(000)	2836	1680	2776	2032	988	4208	4464
cryst size (mm)	0.40 × 0.30 × 0.30	0.25 × 0.25 × 0.13	0.34 × 0.30 × 0.27	0.35 × 0.20 × 0.20	0.33 × 0.12 × 0.12	0.12 × 0.12 × 0.08	0.40 × 0.40 × 0.30
θ range (deg)	3.62−26.00	2.64−29.33	2.64−29.31	2.66−29.31	2.70−29.23	2.54−29.34	3.38−25.00
no. of collected/unique rflns	59 177/15 681 (R(int) = 0.0724)	20 882/10 752 (R(int) = 0.0929)	42077/18 400 (R(int) = 0.0575)	27 432/12 998 (R(int) = 0.0603)	13 317/8176 (R(int) = 0.1890)	97 466/54 121 (R(int) = 0.0891)	82 570/20 347 (R(int) = 0.1060)
no. of data/restraints/params	15 681/15/870	10 752/0/513	18 400/0/811	12998/0/578	8176/1/276	54 121/0/2506	20 347/1/1359
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0652, 0.1515	0.0558, 0.0822	0.0596, 0.1344	0.0680, 0.1520	0.0548, 0.0556	0.1154, 0.2944	0.0678, 0.1055
R1, wR2 (all data)[a]	0.1379, 0.1899	0.2481, 0.1055	0.1404, 0.1524	0.1662, 0.1700	0.2792, 0.0833	0.3075, 0.3484	0.1300, 0.1268
GOF	0.980	0.685	0.898	0.819	0.553	0.857	0.952
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.397/−0.224	0.246/−0.195	0.548/−0.515	0.776/−0.467	0.235/−0.230	1.119/−2.084	0.202/−0.195

[a] $R1 = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{0.5}$.

12H, CH(C*H*$_3$)$_2$), 3.38 (m, 4H, C*H*(CH$_3$)$_2$), 3.99 (m, 4H, C*H*(CH$_3$)$_2$), 6.72 (m, 8H, Ar H), 7.00 (m, 4H, Ar H), 7.12 (m, 12H, Ar H), 7.42 (m, 8H, Ar H). Anal. Calcd for $C_{82.5}H_{106}Al_4N_8$: C, 75.20; H, 8.11; N, 8.50. Found: C, 75.01; H, 7.09; N, 8.17.

With TbpCN (1:1 Ratio). **2** (2.00 g, 4.3 mmol), TbpCN (0.68 g, 4.3 mmol), hexane (20 mL). The filtrate was allowed to evaporate slowly under nitrogen to obtain an initial crop of colorless crystals of **4** (0.10 g), and further evaporation of the mother liquor gave yellow crystals of **5** (0.64 g, 25%). Characterization data for **4** are as follows. Mp: 190 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ −1.11 (s, 6H, AlMe), 0.20 (s, 6H, AlMe), 0.86 (d, 6H, CH(C*H*$_3$)$_2$), 0.95 (d, 6H, CH(C*H*$_3$)$_2$), 1.00 (s, 18H, C(C*H*$_3$)$_3$), 1.13 (d, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, 12H, CH(C*H*$_3$)$_2$), 1.21 (m, 18H, CH(C*H*$_3$)$_2$), 1.30 (m, 12H, CH(C*H*$_3$)$_2$), 1.36 (d, 6H, CH(C*H*$_3$)$_2$), 1.87 (d, 6H, CH(C*H*$_3$)$_2$), 2.65 (m, 2H, C*H*(CH$_3$)$_2$), 2.99 (m, 2H, C*H*(CH$_3$)$_2$), 3.26 (m, 2H, C*H*(CH$_3$)$_2$), 3.43 (m, 2H, C*H*(CH$_3$)$_2$), 3.53 (m, 2H, C*H*(CH$_3$)$_2$), 3.86 (m, 4H, NH and C*H*(CH$_3$)$_2$), 4.35 (m, 2H, NH), 6.62 (m, 4H, Ar H), 6.85 (m, 8H, Ar H), 7.08 (m, 8H, Ar H), 7.26 (m, 4H, Ar H), 7.80 (m, 2H, Ar H). Characterization data for **5** are as follows. Mp: 270 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ −0.08 (s, 6H, AlMe), 0.39 (m, 12H, AlMe and CH(C*H*$_3$)$_2$), 0.80 (br, 6H, CH(C*H*$_3$)$_2$), 0.89 (m, 12H, CH(C*H*$_3$)$_2$), 0.99 (s, 18H, C(C*H*$_3$)$_3$), 1.31 (br, 6H, CH(C*H*$_3$)$_2$), 1.46 (m, 12H, CH(C*H*$_3$)$_2$), 1.54 (br, 6H, CH(C*H*$_3$)$_2$), 2.72 (br, 2H, C*H*(CH$_3$)$_2$), 2.92 (m, 2H, C*H*(CH$_3$)$_2$), 3.16 (br, 2H, C*H*(CH$_3$)$_2$), 3.96 (m, 2H, C*H*(CH$_3$)$_2$), 6.80 (m, 4H, Ar H), 6.98 (m, 4H, Ar H), 7.10 (m, 4H, Ar H), 7.26 (d, 4H, Ar H), 7.95 (d, 4H, Ar H). Anal. Calcd for $C_{74}H_{106}Al_4N_6$: C, 74.84; H, 9.00; N, 7.08. Found: C, 74.28; H, 9.08; N, 7.00.

With TbpCN (1:2 Ratio). **2** (0.50 g, 1.1 mmol), TbpCN (0.34 g, 2.1 mmol), hexane (15 mL). The filtrate afforded colorless crystals of **6** (0.15 g, 19%) in a few hours at room temperature. Mp: >300 °C dec. Anal. Calcd for $C_{96}H_{132}Al_4N_8$: C, 76.56; H, 8.83; N, 7.44. Found: C, 76.14; H, 8.85; N, 7.22.

With DmpCN. **2** (0.51 g, 1.1 mmol), DmpCN (0.14 g, 1.1 mmol), hexane (15 mL). Colorless crystals of **7a** (0.29 g, 43%) were obtained by storing the filtrate for 2 days at room temperature. Mp: >300 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ −1.14 (s, 9H, AlMe), 1.18 (d, 36H, CH(C*H*$_3$)$_2$), 2.46 (s, 12H, CH$_3$), 3.99 (m, 6H, C*H*(CH$_3$)$_2$), 6.87 (t, 3H, Ar H), 7.00 (d, 6H, Ar H), 7.18 (d, 4H, Ar H), 7.47 (t, 2H, Ar H). Anal. Calcd for $C_{57}H_{78}Al_3N_5$: C, 74.89; H, 8.60; N, 7.66. Found: C, 74.18; H, 8.60; N, 7.37.

With DepCN. **2** (0.30 g, 0.6 mmol), DepCN (0.10 g, 0.6 mmol), hexane (10 mL). Keeping the filtrate at room temperature for 2 days afforded colorless crystals of **7b** (0.15 g, 38%). Mp: >300 °C dec. ^{1}H NMR (400 MHz, C_6D_6): δ −0.55 (s, 9H, AlMe), 0.97 (t, 12H, C*H*$_2$CH$_3$), 1.41 (d, 36H, CH(C*H*$_3$)$_2$), 2.44 (q, 8H, CH$_2$C*H*$_3$), 4.41 (m, 6H, C*H*(CH$_3$)$_2$), 6.54 (d, 4H, Ar H), 6.85 (t, 2H, Ar H), 7.07 (t, 3H, Ar H), 7.21 (d, 6H, Ar H). Anal. Calcd for $C_{61}H_{86}Al_3N_5$: C, 75.51; H, 8.93; N, 7.22. Found: C, 75.11; H, 8.95; N, 7.01.

With DippCN. **2** (0.51 g, 1.1 mmol), DippCN (0.20 g, 1.1 mmol), hexane (10 mL). Large blocks of colorless crystals of **7c** (0.09 g, 12%) were obtained from the filtrate at room temperatue after 1 day. Mp: >300 °C dec. ^{1}H NMR (400.13 MHz, C_6D_6): δ −0.63 (s, 9H, AlMe), 1.05 (d, 24H, CH(C*H*$_3$)$_2$), 1.37 (d, 36H, CH(C*H*$_3$)$_2$), 3.16 (m, 4H, C*H*(CH$_3$)$_2$), 4.40 (m, 6H, C*H*(CH$_3$)$_2$), 6.77 (d, 4H, Ar H), 7.02 (t, 2H, Ar H), 7.07 (t, 3H, Ar H), 7.22 (d, 6H, Ar H). Anal. Calcd for $C_{65}H_{94}Al_3N_5$: C, 76.06; H, 9.23; N, 6.82. Found: C, 75.12; H, 9.44; N, 6.77.

Synthesis of *N*-(Dipp)benzamidine. Recently, a synthetic procedure for this compound was reported.[19] However, we adopted a literature procedure published for the preparation of *N*-phenylbenzamidine.[20] To a mixture of 2,6-diisopropylaniline (10.0 g, 56.4 mmol) and benzonitrile (5.8 g, 56.4 mmol) was added AlCl$_3$ (7.5 g, 56.4 mmol) at 0 °C. The mixture was stirred at this temperature for 10 min and heated at 200 °C for 4 h. The molten mixture was poured into a thoroughly mixed solution of 3.2 mL of HCl and 250 mL of H$_2$O. After the addition of 3.2 g of activated carbon the suspension was stirred for 15 min and filtered. The filtrate was treated with NaOH solution (35 g in 200 mL of water) to precipitate the crude product, which was filtered and dried in air for several hours. The compound was recrystallized from a hexane/toluene mixture. Yield: 10.5 g (66%). Mp: 159−160 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.28 (dd, 12H, CH(C*H*$_3$)$_2$), 3.07 (m, 2H, C*H*(CH$_3$)$_2$), 4.63 (s, 2H, NH), 7.11 (m, 1H, Ar H), 7.19 (m, 2H, Ar H), 7.47 (m, 3H, Ar H), 7.94 (m, 2H, Ar H).

Synthesis of 3 from *N*-(Dipp)benzamidine. To *N*-(Dipp)benzamidine (0.46 g, 1.6 mmol) placed in a Schlenk flask was added a solution of AlMe$_3$ (0.82 mL, 1.6 mmol, 2 M in toluene); the mixture was stirred well for 10 min and the flask placed in an oil bath heated at 150 °C for 3 h. The crystalline material was dissolved in toluene and the solution filtered. When it was cooled to 0 °C, the filtrate gave **3** (0.44 g, 88%) as colorless crystals overnight.

Synthesis of 7a−c from Alumazene. A mixture of **1** (1 equiv) and 2,6-dialkylbenzonitrile (2 equiv) was stirred in toluene at room temperatuer for 1 h and filtered, vthe olatiles were removed under vacuum, and the residue was dissolved in the minimum amount of hexane. The crystalline material, which crashed out of solution instantaneously, was separated out and washed further with cold hexane.

7a: **1** (0.46 g, 0.71 mmol), DmpCN (0.27 g, 0.21 mmol). Yield: 0.39 g (60%).

7b: **1** (0.30 g, 0.46 mmol), DepCN (0.15 g, 0.92 mmol). Yield: 0.32 g (77%).

7c: **1** (0.51 g, 0.8 mmol), DippCN (0.29 g, 1.6 mmol). Yield: 0.42 g (52%).

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Supporting Information Available: CIF files giving crystallographic data for **3**−**6** and **7a**−**c** and a listing giving ^{13}C NMR data for all the compounds (except for **6**) reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

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