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Syntheses and Structures of Bis-Amidinate−Alane Complexes

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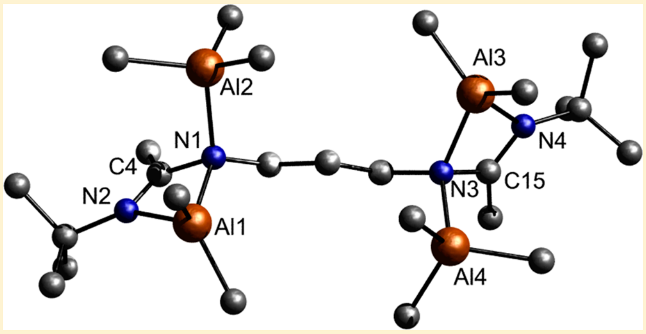
Supporting Information



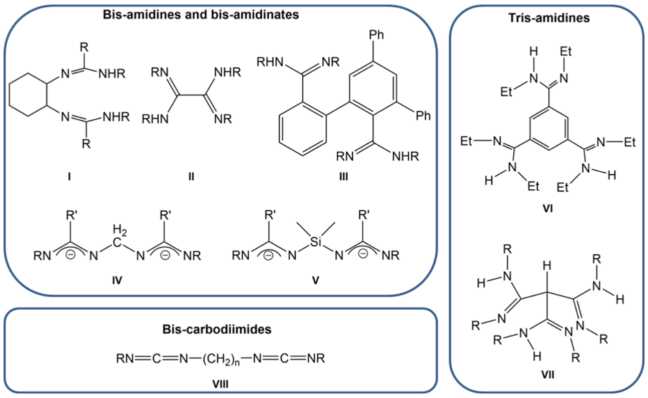
ABSTRACT: Insertion reactions of *α*,*ω*-bis-carbodiimides $(RNCN)_2X$ (**1**−**5**: R = Et, *t*-Bu, Ph; X = C_3H_6, C_4H_8) with 2 equiv of $AlMe_3$ yielded the dinuclear tethered bis-amidinate−alane complexes $[RNC(Me)NAlMe_2]_2X$ (R = Et, X = C_4H_8 (**6**); R = *t*-Bu, X = C_3H_6 (**7**), C_4H_8 (**8**)). Analogous reactions with 4 equiv of $AlMe_3$ resulted in the coordination of two additional $AlMe_3$ molecules, yielding the tetranuclear bis-amidinate complexes $[EtN(AlMe_3)C(Me)NAlMe_2]_2X$ (X = C_3H_6 (**9**), C_4H_8 (**10**)) and $[t\text{-}BuNC(Me)N(AlMe_3)AlMe_2]_2X$ (X = C_3H_6 (**11**), C_4H_8 (**12**)). In addition, equimolar reactions between $(RNCN)_2X$ (R = Et, X = C_3H_6, C_4H_8; R = Ph, X = C_4H_8) and 2 equiv of $AlMe_3$ at elevated temperatures occurred with intramolecular cyclization and formation of $[EtNC(Me)NC_3H_6N(AlMe_3)CNEt]AlMe_2$ (**13**) and $[RNC(Me)NC_4H_8N(AlMe_3)CNR]AlMe_2$ (R = Et (**14**), Ph (**15**)). Hydrolysis of **11** gave the protonated free ligand $PhNC(Me)NC_4H_8N(H)CNPh$ (**16**) in high yield. **6**−**16** were characterized by elemental analyses, multinuclear NMR (^1H, ^{13}C) and IR spectroscopy, and single-crystal X-ray diffraction (**7**, **10**−**14**, **16**).

INTRODUCTION

Bimetallic metal organic complexes, in which two active metal centers are tethered within a single molecule, have received increasing attention within the last decades due to their promising technical application in catalysis.[1] They are expected to provide new reactivity patterns by cooperative electronic effects between the (different) metal atoms which are in close proximity to one another, enhancing the catalytic activity as well as selectivity of multimetallic complexes. As a consequence, several homobimetallic and heterobimetallic complexes have been investigated in the past for catalytic reactions such as asymmetric aldol condensation, olefin polymerization, and ROP of lactide as well as alternating copolymerization of epoxides with CO_2.[2]

Ligand design plays a crucial role in the synthesis of tailor-made complexes containing a bridging unit that allows precise adjustment of the metal−metal separation. Several multifunctional ligands such as bidentate N,N′-chelating monoanionic amidinates, guanidinates, *β*-diketiminates, and N,O-chelating dianionic phenoxyamido ligands as well as tridentate ligands such as tris(pyrazolyl)methanes, triazacyclohexanes, tris(imidazoles), and *β*-triketimines have been established in the past for the synthesis of such multinuclear complexes.[3,4] In addition, bis-amidines of the type $1,4\text{-}C_6H_4[C\{NSiMe_3\}\{N(SiMe_3)_2\}]_2$,[5] $1,4\text{-}C_6H_4[C\{NR\}\{N(H)R\}]_2$,[6] $1,2\text{-}[NC(Ph)N(H)R]_2C_6H_{10}$ (**I**),[7] $[PhN(NH\text{-}t\text{-}Bu)C]_2$ (**II**),[8] and $1\text{-}[C(NR)N(H)R]\text{-}2,4\text{-}Ph_2\text{-}6\text{-}[2\text{-}[C(NR)N(H)R]C_6H_4]C_6H_2$ (**III**)[9] have been used as multifunctional ligand systems and several metal complexes were reported (Scheme 1). Moreover, CH_2-bridged $[H_2C\{NC(Ph)NR\}_2]Li_2$ (**IV**)[10] and $SiMe_2$-bridged bis-amidinates $[Me_2Si\{NC(Ph)NR\}_2]Li_2$ (**V**)[11] as well as tris-amidines of type **VI**[12] have been prepared. Very recently, we synthesized methanetris-amidines of type **VII**[13] by hydrolysis of the corresponding tetranuclear zinc amidinate complexes $\{C[C(NR)_2ZnMe]_4\}$[14] and reported on their capability to form dinuclear, trinuclear, and tetranuclear homometallic complexes as well as heterobimetallic tetranuclear complexes in metalation reactions with $ZnMe_2$, $AlMe_3$, $GaMe_3$, and *i*-Bu_2AlH, respectively.[13,15]

Scheme 1. Bis- and Tris-Amidines as well as Spacer-Bridged Bis-Carbodiimines



C_xH_{2x}-bridged *α*,*ω*-bis-carbodiimides $RNCN-X_n-NCNR$ (X_n = C_2H_4, C_3H_6, ...) of type **VIII** are of potential interest for the formation of tethered bimetallic bis-amidinate

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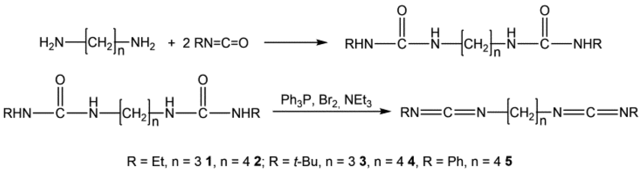
complexes, since they are more flexible in comparison to the CH_2- and $SiMe_2$-bridged systems, which is expected to be a prerequisite for cooperative effects between two metal centers. In principle, ansa-bridged mononuclear bis-amidinates might also be accessible. Early studies showed that α,ω-bis-amidinate complexes can be prepared either by reaction of α,ω-bis-carbodiimides with a transition-metal complex such as $CpTiMe_3$ or by reaction of a lithium salt with a metal halide such as YCl_3.[9,16] Sita et al. reported on the use of bimetallic Zr complexes based on α,ω-bis-amidinates containing different C_nH_{2n} alkyl spacers in olefin polymerization.[17] The results clearly demonstrated the benefit of a dinuclear catalyst, which allowed the stereoselective living coordinative chain transfer polymerization of propene to provide isotactic stereoblock polypropylene (PP), whereas a mononuclear catalyst gave atactic PP.

Herein we report on reactions of different α,ω-bis-carbodiimides with trimethylalane, which proceeded with formation of dinuclear tethered bis-amidinate complexes via insertion of the α,ω-bis-carbodiimides into the Al−Me bond of two $AlMe_3$ molecules. Reactions with 4 equiv of $AlMe_3$ at ambient temperature gave the tetranuclear complexes, in which two additional $AlMe_3$ molecules are coordinated by either the inner or the outer imine center of the amidinate group. Neutral as well as cationic aluminum amidinate complexes have been investigated in the past as catalyst in different catalytic processes[18] such as olefin polymerization[19,20] as well as in the ring-opening polymerization (ROP) of cyclic esters such as lactide and ε-caprolactone.[21]

■ RESULTS AND DISCUSSION

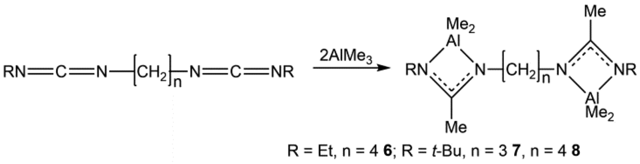
Our attempts to synthesize α,ω-bis-carbodiimides $(RNCN)_2X$ (R = Et, X = C_3H_6 (**1**), C_4H_8 (**2**); R = *t*-Bu, X = C_3H_6 (**3**), C_4H_8 (**4**); R = Ph, X = C_4H_8 (**5**)) by reaction of the corresponding isocyanate with a cyclic bis-amidostannylene as described by Sita et al. gave only very low yields (<20%).[10] We therefore decided to synthesize the α,ω-bis-carbodiimides **1**−**5** by an alternate synthetic route.[17a] In the first step, the corresponding α,ω-bis-ureas are synthesized (Supporting Information), which then react to give the α,ω-bis-carbodiimides **1**−**5** (Scheme 2). Unfortunately, any attempts to obtain **5** in its pure form failed.

Scheme 2. Synthesis of 1−5



Reactions of 2 equiv of $AlMe_3$ with 1 equiv of the α,ω-bis-carbodiimides $(RNCN)_2X$ (R = Et, *t*-Bu; X = C_3H_6, C_4H_8) proceeded with insertion of both carbodiimide groups into the Al−Me bonds of two $AlMe_3$ molecules and formation of the dinuclear α,ω-bis-acetamidinate−alane complexes $[RNC(Me)NAlMe_2]_2X$ (R = Et, X = C_4H_8 (**6**); R = *t*-Bu, X = C_3H_6 (**7**), C_4H_8 (**8**); Scheme 3). The reaction of $(EtNCN)_2C_3H_6$ **1** with 2 equiv of $AlMe_3$ only gave a complex mixture of different compounds, in which complexes **9** and **14** could clearly be identified by ^1H NMR spectroscopy. Additional resonances most likely indicate the formation of $[EtNC(Me)NAlMe_2]_2C_3H_6$, but this compound could not be isolated in its pure form.

Scheme 3. Syntheses of Binuclear Bis-Amidinate Aluminum Complexes 6−8



The NMR spectra of **6**−**8** showed additional resonances due to the C−Me group of the amidinate unit. In addition, the $AlMe_2$ groups were observed as a single resonance in the NMR spectra. The relative intensities of the resonances, which were determined by integration of the signals, of the $AlMe_2$ groups, the R groups (Et, *t*-Bu) of the α,ω-bis-amidinate, and the bridging unit (C_3H_6, C_4H_8) clearly proved the formation of the binuclear complexes **6**−**8**.

Colorless crystals of **7** suitable for single-crystal X-ray diffraction were obtained upon slow evaporation of the solvent of a concentrated toluene solution at ambient temperature for 2 days. **7** crystallizes in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit (Figure 1).

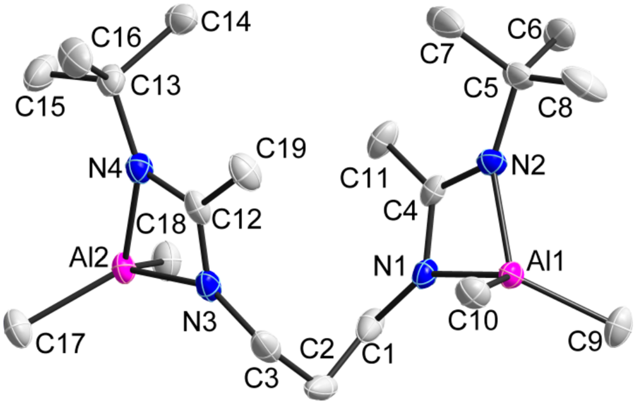


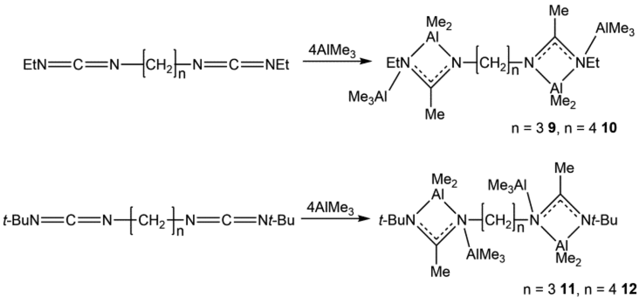
Figure 1. Solid-state structure of **7**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **7**: Al(1)−N(1) 1.9345(13), Al(1)−N(2) 1.9224(12), Al(2)−N(3) 1.9339(13), Al(2)−N(4) 1.9283(14); C(4)−N(1)−C(1) 124.33(13), C(4)−N(1)−Al(1) 90.54(9), C(1)−N(1)−Al(1) 144.94(11), C(4)−N(2)−C(5) 129.26(13), C(4)−N(2)−Al(1) 91.00(9), C(5)−N(2)−Al(1) 139.55(11), C(12)−N(3)−C(3) 124.75(14), C(12)−N(3)−Al(2) 90.56(9), C(3)−N(3)−Al(2) 144.65(12), C(12)−N(4)−C(13) 128.95(13), C(12)−N(4)−Al(2) 90.68(10), C(13)−N(4)−Al(2) 140.21(10); N(3)−C(3)−C(2)−C(1) 55.54(18), C(3)−C(2)−C(1)−N(1) 59.12(17).

The bis-amidinate ligand in **7** acts as an N,N′-chelating ligand to two $AlMe_2$ moieties. The average endocyclic N−C−N (109.76(13)°) and N−Al−N (68.84(6)°) and exocyclic C−Al−C (116.03(8)°) bond angles within the amidinate moieties are comparable to those reported for aluminum amidinate complexes. A CSD database search gave 38 hits on mononuclear aluminum amidinate complexes with the substructure $CC(NC)_2AlC_2$ with bond types set to "any", showing comparable endocyclic N−C−N (average 109.4(18)°) and N−Al−N bond angles (average 68.9(6)°) as well as exocyclic C−Al−C (average 118(2)°) bond angles. In addition, five binuclear bis-amidinate alane complexes have been structurally characterized to date, whose average endocyclic N−C−N (110.27°) and N−Al−N (68.70°) and exocyclic C−Al−C (117.87°) bond angles are comparable.[6,25,26]

Carbodiimide insertion reactions with $AlMe_3$ are known to be a convenient route for the synthesis of aluminum acetamidinate complexes.[22,23] Moreover, reactions with aluminum amides yield the corresponding guanidinate complexes.[24] While mononuclear aluminum amidinate complexes have been prepared in very large numbers, binuclear complexes have been studied to a lesser extent. Hagadorn et al. synthesized dinuclear bis(amidinate) aluminum complexes based on dibenzofuran and 9,9-dimethylxanthene backbones,[25] whereas Coles et al. and Luo et al. reported on 1,4-phenyl- and 1,4-cyclohexyl-bridged binuclear aluminum complexes.[6,26] In addition, structurally related bis-phosphaguanidine aluminum complexes were structurally characterized.[27]

Analogous reactions with 4 equiv of $AlMe_3$ resulted in the coordination of two additional $AlMe_3$ molecules, yielding the tetranuclear bis-amidinate complexes $[EtN(AlMe_3)C(Me)NAlMe_2]_2X$ (X = C_3H_6 (**9**), C_4H_8 (**10**)) and $[t\text{-}BuNC(Me)N(AlMe_3)AlMe_2]_2X$ (X = C_3H_6 (**11**), C_4H_8 (**12**)), respectively (Scheme 4). Jordan et al. reported on the reaction of the comparable thioamidinate alane complex $\{MeC(NAd)S\}AlMe_2$ with $AlMe_3$, which was shown by ^1H NMR spectroscopy to form the corresponding sulfur adduct $\{MeC(NAd)S(AlMe_3)\}AlMe_2$.[28]

Scheme 4. Syntheses of Tetranuclear Bis-Amidinate Aluminum Complexes 9−12



The NMR spectra of **9−12** showed broad resonances of the AlMe moieties in comparison to those obtained for **5−8**, indicating fast exchange reactions on the NMR time scale. However, the relative intensities clearly prove the formation of tetranuclear complexes. Therefore, temperature-dependent ^1H NMR spectra of **10−12** were measured. As an example, Figure 2 shows the ^1H NMR spectra recorded for **11** in the temperature range from −70 to +25 °C. The broad resonance as observed for the AlMe groups at ambient temperature separates into two resonances at 0 °C for the $AlMe_3$ (broad resonance) and the bridging $AlMe_2$ unit (sharp resonance). The latter signal separates upon cooling into two resonances of equal intensity due to the magnetically inequivalent Me groups. The spectrum at −70 °C finally shows three well-resolved resonances in the regime typically observed for AlMe units (−1 to 0 ppm) in a relative intensity of 6:6:18. Comparable findings were observed for **10** and **12**, respectively (see the Supporting Information).

Single crystals of **10−12** were obtained upon storage of solutions in hexane at −30 °C for 24 h.

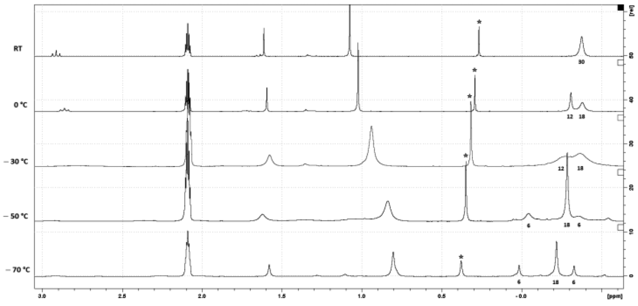


Figure 2. Temperature-dependent ^1H NMR spectra of **11** measured in toluene-d_8 (resonances marked with asterisks are due to grease).

11 crystallizes in the orthorhombic space group *Pbca* with the molecules placed on the general positions (Figure 4). **10** (Figure 3) and **12** (Figure 5) crystallize in a monoclinic lattice (**10**, $P2_1/n$; **12**, $P2_1/c$) with the molecules placed on centers of inversion. The overall conformations of the bridging amidinate ligands are fairly similar; however, because of the odd number of atoms in the linking alkyl chain in **11** and the sp^3 hybridization of the middle atom (i.e., local tetrahedral symmetry) exact centrosymmetry is not possible. The molecular structures are depicted in Figures 3−5. The bis-amidinate ion in **9−12** acts as an N,N′-chelating ligand to the $AlMe_2$ moiety and also as a monodentate σ ligand to a second $AlMe_3$ molecule, thus coordinating two Al atoms per amidinate function. The central alkyl chains show a staggered conformation with torsion angle close to or (because of symmetry) exactly 180°.

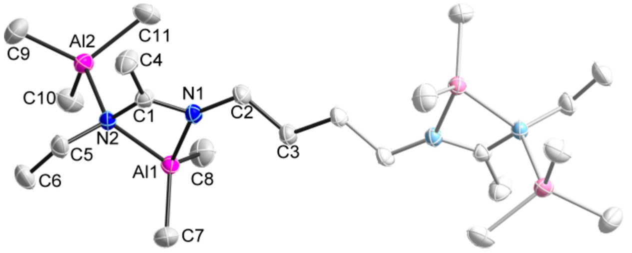


Figure 3. Solid-state structure of **10**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. The pale colored part of the molecule is generated via 1 − *x*, 1 − *y*, 1 − *z*. Selected bond lengths (Å) and angles (deg) of **10**: Al(1)−N(1) 1.9510(11), Al(1)−N(2) 2.0077(11), Al(2)−N(2) 2.0567(11), N(1)−C(1) 1.2873(16), N(1)−C(2) 1.4619(17), N(2)−C(1) 1.4151(17); C(1)−N(1)−C(2) 124.37(11), C(1)−N(1)−Al(1) 93.31(8), C(2)−N(1)−Al(1) 42.20(8), C(1)−N(2)−Al(1) 87.18(7), C(1)−N(2)−Al(2) 109.30(8), Al(1)−N(2)−Al(2) 113.29(5); C(2)−C(3)−C(3)$^{\#2}$−C(2)$^{\#2}$ 180, N(1)−C(2)−C(3)−C(3)$^{\#2}$ −179.79(14).

10−12 show comparable endocyclic N−C−N (**10**, 110.45(11)°; **11**, 109.94(14)°; **12**, 110.00(11)°) and N−Al−N (**10**, 68.24(4)°; **11**, 68.65(10)°; **12**, 68.40(4)°) bond angles within the amidinate moieties as well as exocyclic C−Al−C (**10**, 119.34(7)°; **11**, 119.4(6)°; **12**, 119.61(8)°) bond angles (average values where applicable), which are almost identical with those observed for **7**. The endo- and exocyclic Al−N−C angles differ for the N atoms of the amidinate unit, which can be attributed to the different steric demands of the nonequal residual groups. This observation is in accordance with the Al−N−C bond angles found for asymmetrically substituted aluminum amidinate complexes in the CSD search and to

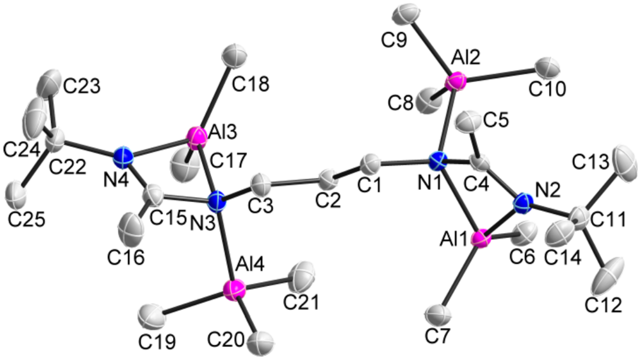


Figure 4. Solid-state structure of **11**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **11**: Al(1)–N(1) 1.9889(19), Al(1)–N(2) 1.950(2), Al(2)–N(1) 2.0655(19), Al(3)–N(4) 1.954(2), Al(3)–N(3) 1.995(2), Al(4)–N(3) 2.053(2), N(1)–C(4) 1.425(3), N(2)–C(4) 1.290(3), N(3)–C(15) 1.431(3), N(4)–C(15) 1.284(3); C(4)–N(1)–Al(1) 87.18(13), C(4)–N(1)–Al(2) 109.37(13), Al(1)–N(1)–Al(2) 114.05(9), C(4)–N(2)–Al(1) 92.73(14), C(15)–N(3)–Al(3) 87.70(14), C(15)–N(3)–Al(4) 112.02(14), Al(3)–N(3)–Al(4) 113.41(10), C(15)–N(4)–Al(3) 93.79(15); N(1)–C(1)–C(2)–C(3) 177.65(18), C(1)–C(2)–C(3)–N(3) −178.56(18).

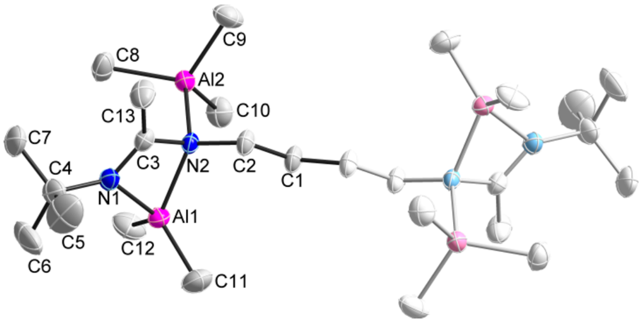


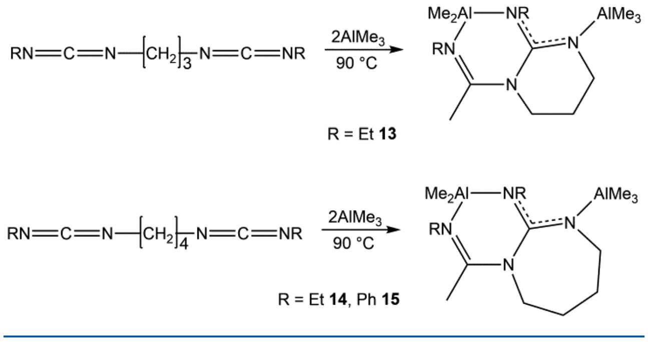
Figure 5. Solid-state structure of **12**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. The pale colored part of the molecule is generated via −*x*, −*y*, 1 − *z*. Selected bond lengths (Å) and angles (deg) of **12**.: Al(1)–N(1) 1.9501(11), Al(1)–N(2) 1.9961(10), Al(2)–N(2) 2.0639(11), N(1)–C(3) 1.2839(16), N(2)–C(3) 1.4225(15), N(2)–C(2) 1.4996(14); C(3)–N(1)–C(4) 130.00(12), C(3)–N(1)–Al(1) 93.36(8), C(4)–N(1)–Al(1) 36.27(9), C(3)–N(2)–C(2) 111.84(9), C(3)–N(2)–Al(1) 87.34(7), C(2)–N(2)–Al(1) 118.67(8), C(3)–N(2)–Al(2) 110.82(7), C(2)–N(2)–Al(2) 112.14(8), Al(1)–N(2)–Al(2) 113.49(5;, C(2)–C(1)–C(1)$^{\#1}$–C-(2)$^{\#1}$ 180, N(2)–C(2)–C(1)–-C(1)$^{\#1}$ 174.49(13).

those reported for the binuclear bis-amidinate alane complexes.[6,25,26]

The most surprising difference among the tetranuclear complexes is revealed by the coordination of the $AlMe_3$ Lewis acid. The additional $AlMe_3$ molecules in **10** are coordinated by the outer $N_{amidinate}$ atom, whereas the inner $N_{amidinate}$ atom binds to the $AlMe_3$ Lewis acid in **11** and **12**. Obviously, the sterically more demanding *t*-Bu groups in **11** and **12** favor the coordination of the $AlMe_3$ molecules to the inner $N_{amidinate}$ atom in order to reduce the steric (repulsive) interactions, whereas the somewhat smaller Et groups in **10** allow the coordination of the $AlMe_3$ molecules by the outer $N_{amidinate}$ atom. Moreover, the *σ*-coordination mode strongly influences the electronic structure of the ligand, since the coordination number of the coordinating N atom increases to 4, resulting in a tetrahedral environment and a change of hybridization from sp^2 to sp^3. As a consequence, the p orbital is no longer available for an electron delocalization within the amidinate group, leading to significantly different C–N bond lengths (**10**, N(1)–C(1) 1.2873(16), N(2)–C(1) 1.4151(17) Å; **11**, N(1)–C(4) 1.425(3), N(2)–C(4) 1.290(3) Å; **12**, N(1)–C(3) 1.2839(16), N(2)–C(3) 1.4225(15) Å) within the amidinate backbone of **10**–**12**. The shorter C–N bond distances are comparable to those reported for N-heteroaromatic compounds (1.336(14) Å)[29] but longer than those reported for carbodiimides (mean value 1.215(4) Å),[30] whereas the longer ones are slightly shorter than those reported for $C(sp^2)$–N single bonds (1.47 Å).[31] In accordance with this finding, the mean Al–$N(sp^3)$ bond lengths (**10**, 1.98(2) Å; **11**, 2.026(17) Å; **12**, 2.03(2) Å) are longer than the mean Al–$N(sp^2)$ lengths (**10**, 1.9510(11) Å; **11**, 1.952(2) Å; **12**, 1.9501(11) Å). These findings are in remarkable contrast to those observed in the mononuclear aluminum amidinate complexes, whose N–C (average 1.340 Å) and N–Al bond lengths (average 1.929 Å) are very similar, indicating almost perfect *π*-delocalization within the amidinate backbone.

We also investigated reactions between $(RNCN)_2X$ (R = Et, X = C_3H_6, C_4H_8; R = Ph, X = C_4H_8) and an equimolar amount of $AlMe_3$ at elevated temperatures in order to investigate the possible formation of an ansa-type complex by twofold insertion of both carbodiimide moieties into two Al–Me bonds of a single $AlMe_3$ molecule. However, these reactions proceeded with intramolecular cyclization due to the nucleophilic attack of the inner amidinate N atom to the electrophilic carbon atom of the second carbodiimide unit and subsequent formation of $[EtNC(Me)NC_3H_6N(AlMe_3)CNEt]AlMe_2$ (**13**) and $[RNC(Me)NC_4H_8N(AlMe_3)CNR]AlMe_2$ (R = Et (**14**), Ph (**15**)), respectively, rather than with formation of the ansa-type complexes (Scheme 5). **13**–**15** were also prepared in higher yields by analogous reaction with 2 equiv of $AlMe_3$ at 90 °C.

Scheme 5. Syntheses of 13–15



The NMR spectra of **13**–**15** each showed two sets of resonances for the different Al–Me groups ($AlMe_2$, $AlMe_3$) in a relative intensity of 2:3. In addition, **13** and **14** also showed two triplets and two quartets for the Et groups. Unfortunately, all attempts to obtain **15** in its pure form failed. The ^1H NMR spectra of different samples always showed additional resonances, which could not be addressed.

Single crystals of **13** and **14** were obtained upon storage of solutions in hexane at −30 °C for 24 h. **13** and **14** (Figures 6 and 7, respectively) crystallize in the monoclinic space groups $P2_1/c$ (**13**) and $P2_1/n$ (**14**). In both molecules, the $AlMe_2$

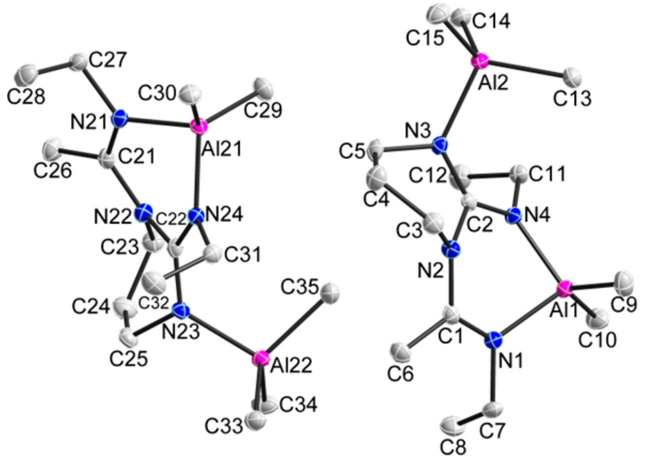


Figure 6. Asymmetric unit of **13**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) for one molecule of **13**: N(1)−C(1) 1.2897(19), N(2)−C(1) 1.3869(19), N(2)−C(2) 1.4168(19), N(2)−C(3) 1.4818(18), N(3)−C(2) 1.3320(19), N(4)−C(2) 1.3210(18); C(1)−N(1)−Al(1) 119.32(10), C(1)−N(2)−C(2) 126.44(12), C(1)−N(2)−C(3) 120.30(12), C(2)−N(2)−C(3) 113.21(11), C(2)−N(4)−Al(1) 120.22(10), N(4)−C(2)−N(2) 118.20(13), N(4)−C(2)−N(3) 126.44(14), N(3)−C(2)−N(2) 115.35(12).

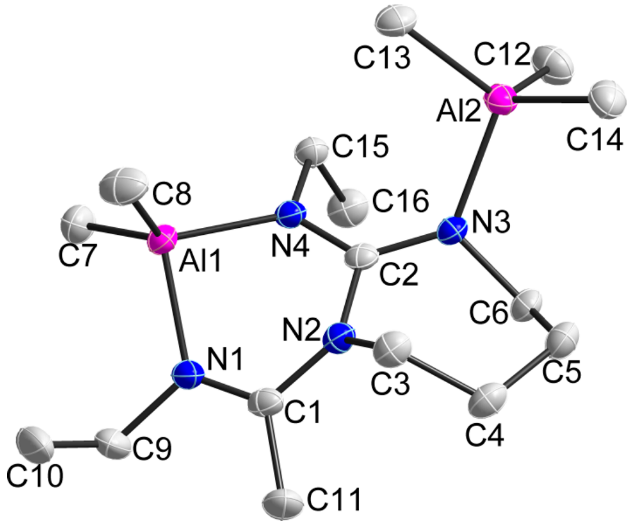
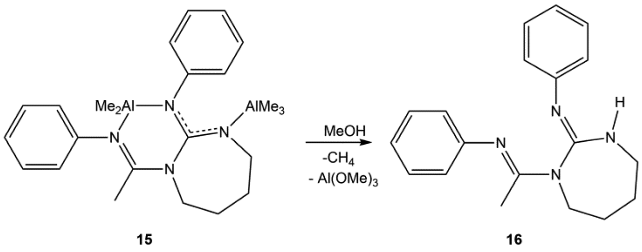


Figure 7. Solid-state structure of **14**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **14**: N(1)−C(1) 1.283(3), N(2)−C(1) 1.394(3), N(2)−C(2) 1.427(3), N(2)−C(3) 1.489(3), N(3)−C(2) 1.330(3), N(4)−C(2) 1.320(3); C(1)−N(1)−Al(1) 119.94(15), C(1)−N(2)−C(2) 125.49(17), C(1)−N(2)−C(3) 117.48(17), C(2)−N(2)−C(3) 116.75(17), C(2)−N(4)−Al(1) 122.24(14), N(1)−C(1)−N(2) 120.58(18), N(4)−C(2)−N(3) 125.39(18), N(4)−C(2)−N(2) 117.06(17), N(3)−C(2)−N(2) 117.55(18).

moieties are κ^2-coordinated by the N,N′-chelating amidinate groups while the AlMe$_3$ groups are σ-bonded. The nitrogen atoms N1−N4 as well as the central C atoms C1 and C2 adopt an almost planar arrangement in both molecules (rms deviation from best plane; **13**, 0.1379 and 0.1281 Å; **14**, 0.4975 Å, C3 and C6 with approximately 1 Å deviate most) and can be best described as sp^2 hybridized. However, the corresponding C−N bond lengths (**13**, N(1)−C(1) 1.2897(19), N(2)−C(1) 1.3869(19), N(2)−C(2) 1.4168(19), N(2)−C(3) 1.4818(18), N(3)−C(2) 1.3320(19), N(4)−C(2) 1.3210(18) Å; **14**, N(1)−C(1) 1.283(3), N(2)−C(1) 1.394(3), N(2)−C(2) 1.427(3), N(2)−C(3) 1.489(3), N(3)−C(2) 1.330(3), N(4)−C(2) 1.320(3) Å) suggest only limited delocalization of the π electrons.

Finally, the raw product of **15** was reacted with an excess of methanol in order to synthesize the free ligand PhNC(Me)-$NC_4H_8N(H)CNPh$ (**16**; Scheme 6). **16** was obtained in the form of X-ray-quality crystals after workup in reasonable yield.

Scheme 6. Synthesis of 16



16 crystallizes in the monoclinic space group $P2_1/n$ (Figure 8). In remarkable contrast to **13** and **14**, the sp^2-hybridized N atoms and the central C atoms C1 and C2 in **16** are far from forming a plane (C1−N1−C2−N3 62.9(2)°). Interestingly, to achieve the cisoid arrangement of the N atoms as observed for **13** and **14**, a rotation around the double bonds (C1═N1, C2═N3) is necessary. However, the N2H−C2−N3 unit shows a strong hydrogen bond (H···A 2.037 Å, D−H···A 170.99°)

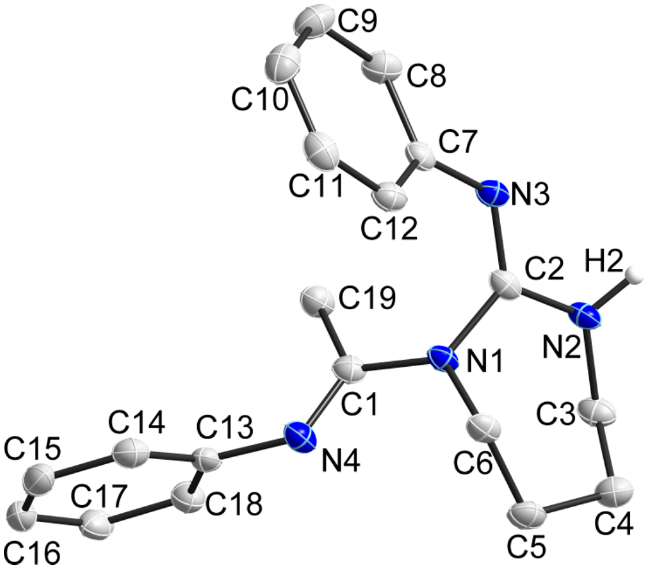


Figure 8. Solid-state structure of **16**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) of **16**: N(1)−C(1) 1.384(2), N(1)−C(2) 1.417(2), N(1)−C(6) 1.472(2), N(2)−C(2) 1.337(2), N(2)−C(3) 1.465(2), N(3)−C(2) 1.294(2), N(3)−C(7) 1.408(2), N(4)−C(1) 1.281(2), N(4)−C(13) 1.416(2); C(1)−N(1)−C(2) 123.96(14), C(1)−N(1)−C(6) 120.19(13), C(2)−N(1)−C(6) 115.85(13), C(2)−N(2)−C(3) 124.96(14), C(2)−N(3)−C(7) 123.33(14), C(1)−N(4)−C(13) 22.03(16), N(4)−C(1)−N(1) 116.84(15), N(4)−C(1)−C(19) 126.79(16), N(1)−C(1)−C(19) 116.37(15), N(3)−C(2)−N(2) 20.17(15), N(3)−C(2)−N(1) 126.12(16), N(2)−C(2)−N(1) 113.67(14).

forming a centrosymmetric $R^2_2(8)$ motif comparable to that found in carbonic acid dimers, which might influence the π system. The different conformation fulfills the steric demands of this interaction and might be a consequence of this interaction.

CONCLUSIONS

A series of dinuclear α,ω-bis-amidinate−alane complexes **6**−**8** have been prepared by the reaction of α,ω-bis-carbodiimides with a twofold amount of $AlMe_3$ at ambient temperature. Reactions with a fourfold amount of $AlMe_3$ yielded tetranuclear bis-amidinate complexes **9**−**12**, in which two additional $AlMe_3$ molecules are coordinated by either the inner or outer imine centers, depending on the steric demand of the organic substituent attached to the outer imine moiety. In addition, cyclization reactions were observed in reactions of α,ω-bis-carbodiimides with 2 equiv of $AlMe_3$ at higher temperatures, yielding **13**−**15**. The free heterocyclic ligands, which can be obtained from hydrolysis reactions of the corresponding alane complexes as was shown for the bis-amidine **16**, might be used in the future in reactions with metal organic complexes containing different metal centers.

EXPERIMENTAL SECTION

General Procedures and Materials. All manipulations were performed in a glovebox (MBraun) under an Ar atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. A 2 M solution of $AlMe_3$ in toluene was obtained from Sigma-Aldrich and used as received. A Bruker DMX 300 was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal deuteriobenzene (C_6D_5H, ^1H δ 7.154; C_6D_6, ^{13}C δ 128.0) and deuteriodichloromethane ($CHDCl_2$, ^1H δ 5.32; CD_2Cl_2, ^{13}C δ 53.84). IR spectra were recorded on a Bruker ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the *Elementaranalyse Labor* of the University of Duisburg-Essen.

General Experimental Procedure for the Synthesis of 1−5. α,ω-Bis-carbodiimides were prepared according to a procedure previously reported by Sita et al. for compound **4**.[17a] The products crystallized from the raw product upon storage at −30 °C. The yields (isolated crystalline products) are based on the bis-ureas, which were prepared in high yields (see the Supporting Information).

*$(EtNCN)_2C_3H_6$ (**1**).* Yield: 2.10 g (43.4%). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ 0.95 (t, 6 H, CH_2CH_3), 1.50 (quint, 2 H, CH_2), 2.92 (quart, 4 H, NCH_2), 3.09 (t, 4 H, CH_2CH_3). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 16.8 (CH_3) 33.0 (CH_2), 41.4 (CH_2CH_3), 43.9 (NCH_2), 140.4 (NCN). IR: ν 2972, 2933, 2871, 2115, 1692, 1631, 1574, 1518, 1489, 1451, 1433, 1403, 1375, 1335, 1308, 1281, 1200, 1131, 1087, 937, 887, 845, 785, 744, 697, 610, 500, 422 cm^{-1}.

*$(EtNCN)_2C_4H_8$ (**2**).* Yield: 2.28 g (51.3%). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ 0.97 (t, 6 H, CH_2CH_3), 1.41 (m, 4 H, CH_2), 2.94 (m, 8 H, NCH_2, CH_2CH_3). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 16.9 (CH_3) 29.0 (CH_2), 41.4 (CH_2CH_3), 46.2 (NCH_2), 140.4 (NCN). IR: ν 2966, 2930, 2867, 2117, 1728, 1649, 1585, 1448, 1434, 1355, 1259, 1157, 1087, 1015, 912, 871, 798, 743, 696, 645, 610, 541, 500, 396 cm^{-1}.

*$(t\text{-}BuNCN)_2C_3H_6$ (**3**).* Yield: 2.70 g (46.2%). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ 1.16 (s, 18 H, CMe_3) 1.56 (m, 2 H, CH_2), 3.12 (m, 4 H, NCH_2, CH_2CH_3). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 31.5 (CH_2), 33.4 ($NCMe_3$), 44.1 (NCH_2), 54.8 ($NCMe_3$), 139.8 (NCN).IR: ν 2952, 2902, 2107, 2061, 1642, 1459, 1392, 1365, 1334, 1309, 1245, 1186, 1083, 1018, 953, 918, 831, 792, 747, 679, 618, 566, 471, 440, 396 cm^{-1}.

*$(t\text{-}BuNCN)_2C_4H_8$ (**4**).* Yield: 2.62 g (47.6%). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ 1.17 (s, 18 H, CMe_3), 1.44 (m, 4 H, CH_2), 2.95 (m, 4 H, NCH_2). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 29.2 (CH_2), 31.5 ($NCMe_3$), 46.5 (NCH_2), 54.7 ($NCMe_3$), 139.9 (NCN). IR: ν 2968, 2930, 2868, 2106, 2061, 1461, 1392, 1365, 1351, 1272, 1237, 1187, 1092, 1015, 975, 922, 778, 671, 618, 541, 446, 386 cm^{-1}.

*$(PhNCN)_2C_4H_8$ (**5**).* Purification of **5** failed. **5** was obtained as a mixture with so far unidentified products. However, some resonances in the ^1H NMR can be most likely attributed to **5**. ^1H NMR (300 MHz, $CHDCl_2$, 25 °C): δ 1.80 (m, 4 H, CH_2), 3.49 (m, 4 H, NCH_2), 7.08 (m, 4 H, Ar) 7.28 (t, 4 H, Ar). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ 28.6 (CH_2), 46.1 (CH_2), 124.0 (*Ar*), 124.9 (*Ar*), 128.5 (*Ar*), 129.7 (*Ar*), 141.3 (NCN).

General Experimental Procedure for the Synthesis of 6−8. A solution of $AlMe_3$ in toluene (**6**, 1.84 mL, 3.6 mmol; **7**, **8**, 1.76 mL, 3.6 mmol) was added at −80 °C to a solution of the corresponding α,ω-bis-carbodiimide (**6**, 0.40 g, 1.8 mmol; **7**, **8**, 0.44 g, 1.8 mmol) in 15 mL of toluene. The solution was warmed to ambient temperature within 12 h. All volatiles were evaporated under vacuum, yielding **6**−**8** as colorless solids. Analytically pure **6**−**8** were obtained upon recrystallization of solutions in hexane/toluene at −30 °C.

*$[EtNC(Me)NAlMe_2]_2C_4H_8$ (**6**).* Yield: 0.50 g (80.3%). Melting point: 81 °C dec. Anal. Found (calcd) for $C_{16}H_{36}Al_2N_4$ (338.44 g/mol): H, 10.60 (10.72); C, 56.90 (56.78). ^1H NMR (300 MHz, $CHDCl_2$, 25 °C): δ −0.76 (s, 12 H, $AlMe_2$), 1.10 (t, 6 H, CH_2CH_3), 1.48 (m, 4 H, CH_2), 1.98 (s, 6 H, CMe), 3.13 (m, 4 H, CH_2CH_3), 3.18 (quart, 4 H, CH_2). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ −8.2 ($AlMe_2$), 12.3 (CH_3), 16.4 (CMe), 29.3 (CH_2), 40.4 (CH_2), 45.7 (CH_2), 178.2 (NCN). IR: ν 2974, 2926, 2886, 2817, 1625, 1528, 1466, 1389, 1243, 1184, 1156, 1105, 1054, 992, 932, 908, 827, 678, 621, 585, 524, 474, 417, 385 cm^{-1}.

*$[t\text{-}BuNC(Me)NAlMe_2]_2C_3H_6$ (**7**).* Yield: 0.57 g (83.2%). Melting point: 118 °C dec. Anal. Found (calcd) for $C_{19}H_{42}Al_2N_4$ (380.52 g/mol): H, 10.78 (11.12); C, 60.30 (59.97). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ −0.25 (s, 12 H, $AlMe_2$), 1.08 (s, 18 H, CMe_3), 1.52 (s, 6 H, CMe), 1.57 (t, 2 H, CH_2), 2.91 (t, 4 H, NCH_2). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ −9.6 ($AlMe_2$), 14.1 (CMe), 31.5 ($NCMe_3$), 33.3 (CH_2), 42.0 (NCH_2), 50.4 ($NCMe_3$), 173.9 (NCN). IR: ν 2966, 2928, 2885, 1653, 1606, 1492, 1452, 1415, 1362, 1334, 1314, 1265, 1221, 1182, 1095, 1028, 845, 794, 676, 589, 537, 434, 381 cm^{-1}.

*$[t\text{-}BuNC(Me)NAlMe_2]_2C_4H_8$ (**8**).* Yield: 0.58 g (81.7%). Melting point: 121.4 °C dec. Anal. Found (calcd) for $C_{20}H_{44}Al_2N_4$ (394.55 g/mol): H, 10.9 (11.24); C, 59.00 (60.88). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ −0.25 (s, 12 H, $AlMe_2$), 1.09 (s, 18 H, CMe_3), 1.44 (m, 4 H, NCH_2), 1.48 (s, 6 H, CMe), 2.79 (m, 4 H, CH_2). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ −9.5 ($AlMe_2$), 14.0 (CMe), 29.8 (CH_2), 31.5 ($NCMe_3$), 44.3 (NCH_2), 50.3 ($NCMe_3$), 173.6 (NCN). IR: ν 2925, 2860, 1653, 1508, 1483, 1439, 1421, 1359, 1249, 1183, 1069, 1035, 1021, 820, 785, 685, 654, 623, 590, 556, 476, 442, 396 cm^{-1}.

General Experimental Procedure for the Synthesis of 9−12. A solution of $AlMe_3$ in toluene (**9**, **10**, 3.68 mL, 7.2 mmol; **11**, **12**, 3.52 mL, 7.2 mmol) was added at room temperature to a solution of the α,ω-bis-carbodiimide (**9**, **10**, 0.40 g, 1.8 mmol; **11**, **12**, 0.44 g 1.8 mmol) in 15 mL of hexane and stirred for 15 min. All volatiles were evaporated under vacuum, yielding **9**−**12** as colorless solids. Analytically pure **9**−**12** were obtained upon recrystallization of solutions in toluene at −30 °C.

*$[EtN(AlMe_3)C(Me)NAlMe_2]_2C_3H_6$ (**9**).* The samples always contained mixtures of **9** and **13** (35:65). Fractionated crystallization from a solution in toluene yielded pure **9**. Melting point: 82 °C dec. Anal. Found (calcd) for $C_{21}H_{52}Al_4N_4$ (468.58 g/mol): H, 10.90 (11.18); C, 53.48 (53.82). ^1H NMR (300 MHz, C_6D_6H, 25 °C): δ −0.27 (bs, 30 H, AlMe), 0.91 (t, 6 H, CH_2CH_3), 1.33 (bs, 8 H, CH_2, CMe), 2.77 (m, 8 H, CH_2CH_3, CH_2). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ −11.1 (AlMe), −7.0 (AlMe), 13.4 (CH_3), 15.9 (CH_3), 32.2 (CH_2), 41.5 (CH_2), 47.2 (CH_2), 179.6 (NCN). IR: ν 2962, 2920, 2884, 2820, 1663, 1620, 1524, 1437, 1342, 1260, 1176, 1121, 1083, 1025, 796, 727, 679, 616, 537, 511, 442, 392 cm^{-1}.

*$[EtN(AlMe_3)C(Me)NAlMe_2]_2C_4H_8$ (**10**).* Yield: 0.77 g (88.6%). Melting point: 84 °C dec. Anal. Found (calcd) for $C_{22}H_{54}Al_4N_4$ (482.61 g/mol): H, 10.93 (11.28); C, 54.34 (54.75). ^1H NMR (300 MHz, $CHDCl_2$, 25 °C): δ −0.67 (s (br), 30 H, $AlMe_2$), 1.14 (t, 6 H,

CH$_2$C*H*$_3$), 1.53 (m, 4 H, C*H*$_2$), 2.05 (s, 6 H, C*Me*), 3.15 (m, 4 H, C*H*$_2$CH$_3$), 3.18 (q, 4 H, C*H*$_2$). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ −11.5 (Al*Me*), −7.6 (Al*Me*), 16.0 (C*Me*), 29.1 (CH$_2$), 30.4 (CH$_3$), 41.1 (CH$_2$), 46.3 (CH$_2$), 176.8 (NCN). IR: ν 2963, 2926, 2886, 2819, 1625, 1526, 1437, 1343, 1281, 1260, 1184, 1157, 1082, 1016, 857, 790, 744, 675, 538, 524, 496, 474, 385 cm^{-1}.

[t-BuN(AlMe$_3$)C(Me)NAlMe$_2$]$_2$C$_3$H$_6$ ***(11)***. Yield: 0.84 g (88.9%). Melting point: 126.0 °C dec. Anal. Found (calcd) for C$_{25}$H$_{60}$Al$_4$N$_4$ (524.69 g/mol): H, 11.33 (11.5); C, 55.97 (57.2). ^{1}H NMR (300 MHz, C$_6$D$_6$H, 25 °C): δ −0.35 (s, 18 H, Al*Me*$_3$), −0.30 (s, 12 H, Al*Me*$_2$), 1.02 (s, 18 H, C*Me*$_3$), 1.59 (s, 6 H, C*Me*), 1.72 (quint, 2 H, CH$_2$C*H*$_2$CH$_2$), 2.87 (m, 4 H, C*H*$_2$).^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ −9.3 (Al*Me*$_3$), −6.6 (Al*Me*$_2$), 14.8 (C*Me*), 31.0 (C*Me*$_3$), 32.5 (CH$_2$), 43.1 (CH$_2$), 51.1 (CMe$_3$), 175.7 (CNC). IR: ν 2968, 2928, 2884, 2819, 1611, 1496, 1475, 1398, 1371, 1266, 1188, 1128, 1099, 1081, 1038, 988, 938, 915, 839, 798, 678, 618, 522, 436, 391 cm^{-1}.

[t-BuN(AlMe$_3$)C(Me)NAlMe$_2$]$_2$C$_4$H$_8$ ***(12)***. Yield: 0.87 g (89.8%). Melting point: 127.0 °C dec. Anal. Found (calcd) for C$_{26}$H$_{62}$Al$_4$N$_4$ (538.72 g/mol): H, 11.41 (11.60); C, 58.05 (57.97). ^{1}H NMR (300 MHz, C$_6$D$_6$H, 25 °C): δ −0.35 (s, 18 H, Al*Me*$_3$), −0.26 (s, 12 H, Al*Me*$_2$), 1.04 (s, 18 H, C*Me*$_3$), 1.52 (m, 10 H, C*H*$_2$, CC*H*$_3$), 2.79 (m, 4 H, NC*H*$_2$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ −9.1 (Al*Me*$_3$), −6.6 (Al*Me*$_2$), 15.1 (C*Me*), 29.4 (CH$_2$), 30.9 (NC*Me*$_3$), 45.6 (NC*H*$_2$), 51.4 (NCMe$_3$), 176.2 (NCN). IR: ν 2957, 2924, 2886, 2871, 2819, 1613, 1474, 1371, 1268, 1219, 1195, 1180, 1092, 1038, 982, 933, 845, 799, 682, 624, 595, 524, 483, 437, 394 cm^{-1}.

General Experimental Procedure for the Synthesis of 13−15. A solution of AlMe$_3$ in toluene (**9**, 1.76 mL, 3.6 mmol; **10**, 1.84 mL, 3.6 mmol; **11**, 1.76 mL, 2.8 mmol) was added to a solution of the α,ω-bis-carbodiimide (**9**, 0.40 g, 1.8 mmol; **10**, 0.40 g, 1.8 mmol; **11**, 0.40 g, 1.4 mmol) in 15 mL of toluene, and the mixture was heated to 90 °C and stirred for 15 min. All volatiles were evaporated under vacuum after the solution was cooled to ambient temperature, yielding **13−15** as colorless crystalline solids. Analytically pure **13** and **14** were obtained upon recrystallization of solutions in hexane/toluene at −30 °C.

[EtNC(Me)NC$_3$H$_6$N(AlMe$_3$)CNEt]AlMe$_2$ ***(13)***. Yield: 0.52 g (89.0%). Melting point: 96 °C dec. Anal. Found (calcd) for C$_{15}$H$_{34}$Al$_2$N$_4$ (324.42 g/mol): H, 10.32 (10.56); C, 55.18 (55.53). ^{1}H NMR (300 MHz, C$_6$D$_6$H, 25 °C): δ −0.55 (s, 6 H, Al*Me*$_2$), −0.21 (s, 9 H, Al*Me*$_3$), 0.61 (t, 3 H, CH$_2$C*H*$_3$), 0.96 (s, 3 H, C*Me*), 1.04 (t, 3 H, CH$_2$C*H*$_3$), 1.62 (quint, 2 H, C*H*$_2$), 2.64 (q, 2 H, C*H*$_2$), 2.74 (t, 2 H, C*H*$_2$), 3.07 (t, 2 H, C*H*$_2$), 3.67 (q, 2 H, C*H*$_2$). ^{13}C NMR (75 MHz, C$_6$D$_6$, 25 °C): δ −11.1 (Al*Me*$_2$), −6.7 (Al*Me*$_2$), 14.6 (CH$_3$), 15.7 (CH$_3$), 16.2 (CH$_3$), 41.1 (CH$_2$), 41.5 (CH$_2$), 42.9 (CH$_2$), 44.7 (CH$_2$), 163.8 (NCN), 165.3 (NCN). IR: ν 2977, 2919, 2883, 2816, 1664, 1618, 1563, 1475, 1461, 1438, 1379, 1338, 1312, 1268, 1175, 1115, 1082, 1064, 1027, 983, 936, 921, 903, 876, 838, 800, 746, 670, 613, 577, 523, 398 cm^{-1}.

[EtNC(Me)NC$_4$H$_8$N(AlMe$_3$)CNEt]AlMe$_2$ ***(14)***. Yield: 0.53 g (85.2%). Melting point: 98 °C dec. Anal. Found (calcd) for C$_{16}$H$_{36}$Al$_2$N$_4$ (338.44 g/mol): H, 10.54 (10.72); C, 56.35 (56.78). ^{1}H NMR (300 MHz, CHDCl$_2$, 25 °C): δ −1.00 (s, 9 H, Al*Me*$_3$), −0.83 (s, 6 H, Al*Me*$_2$), 0.92 (t, 3 H, CH$_2$C*H*$_3$), 1.22 (t, 3 H, CH$_2$C*H*$_3$), 1.76 (m, 4 H, C*H*$_2$), 2.47 (s, 3 H, C*Me*), 3.47−3.50 (m, 6 H, C*H*$_2$CH$_3$, C*H*$_2$). ^{13}C NMR (125 MHz, CD$_2$Cl$_2$, 25 °C): δ −11.5 (Al*Me*$_3$), −7.0 (Al*Me*$_2$), 15.0 (CH$_3$), 16.2 (CH$_3$), 17.6 (CH$_3$), 27.0 (CH$_2$), 27.6 (CH$_2$), 43.0 (CH$_2$), 43.7 (CH$_2$), 49.3 (CH$_2$), 52.0 (CH$_2$), 164.3 (NCN), 168.8 (NCN). IR: ν 2966, 2923, 2884, 2816, 1657, 1616, 1559, 1449, 1376, 1341, 1324, 1265, 1183, 1116, 1064, 1038, 920, 871, 793, 678, 627, 588, 515, 441 cm^{-1}.

[PhNC(Me)NC$_4$H$_8$N(AlMe$_3$)CNPh]AlMe$_2$ ***(15)***. Any attempts to purify **15** failed. The ^{1}H NMR spectrum always showed additional resonances aside from those, which were addressed to **15**. ^{1}H NMR (300 MHz, CHDCl$_2$, 25 °C): δ −1.38 (s, 6 H, Al*Me*$_3$), −1.07 (s, 9 H, Al*Me*$_2$), 1.85 (m, 4 H, C*H*$_2$), 2.32 (s, 3 H, C*Me*), 3.30 (m, 2 H, C*H*$_2$), 3.73 (m, 2 H, C*H*$_2$), 6.93 (t, 2 H, *Ar*), 6.96 (d, 2 H, *Ar*), 7.08 (t, 2 H, *Ar*), 7.24 (t, 2 H, *Ar*), 7.44 (t, 2 H, *Ar*).

Synthesis of 16. MeOH (0.20 mL, 5 mmol) was added at ambient temperature to the raw product of **15** (0.44 g, 1 mmol), and the mixture was stirred for 30 min. MeOH was then evaporated under vacuum, yielding a white solid, from which analytically pure **16** was isolated after extraction with CH$_2$Cl$_2$ followed by evaporation of the solvent.

PhNC(Me)NC$_4$H$_8$N(H)CNPh ***(16)***. Yield: 0.14 g (48%). Melting point: 145.5 °C dec. Anal. Found (calcd) for C$_{19}$H$_{22}$N$_4$ (306.41 g/mol): H, 7.18 (7.24); C, 74.37 (74.48). ^{1}H NMR (300 MHz, CHDCl$_2$, 25 °C): δ 1.62 (m, 2 H, C*H*$_2$), 1.77 (m, 2 H, C*H*$_2$), 2.09 (s, 3 H, C*Me*), 3.28 (m, 2 H, C*H*$_2$), 3.95 (m, 2 H, C*H*$_2$), 4.77 (s, 1 H, N*H*), 6.75 (d, 2 H, *Ar*), 6.88 (d, 2 H, *Ar*), 7.00 (m, 2 H, *Ar*), 7.21−7.34 (t, 4 H, *Ar*). ^{13}C NMR (75 MHz, CD$_2$Cl$_2$, 25 °C): δ 17.9 (C*Me*$_3$), 27.1 (CH$_2$), 29.5 (CH$_2$), 44.1 (CH$_2$), 45.7 (CH$_2$), 121.4 (Ar), 121.8 (Ar), 122.3 (Ar), 123.0 (Ar), 129.0 (Ar), 129.2 (Ar), 130.0 (Ar). IR: ν 3677, 2962, 2909, 2827, 2783, 1650, 1611, 1584, 1506, 1472, 1456, 1412, 1367, 1339, 1281, 1259, 1189, 1088, 1067, 1012, 928, 859, 794, 732, 692, 388 cm^{-1}.

Single-Crystal X-ray Analyses. Crystallographic data of **7**, **10−14** and **16**, which were collected on a Bruker AXS SMART diffractometer (Mo Kα radiation, λ = 0.71073 Å) at low temperatures, are summarized in Table 1 in the Supporting Information. The solid-state structures of **7**, **10−14**, and **16** are shown in Figures 1 and 3−8, respectively. The structures were solved by direct methods (SHELXS-97) and refined anisotropically by full-matrix least squares on F^2 (SHELXL-97).[32,33] **14** was a pseudomerohedral twin and was refined accordingly. The major component comprised approximately 90% of the sample. Absorption corrections were performed semiempirically from equivalent reflections on the basis of multiscans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. The crystallographic data of **7**, **10−14**, and **16** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-992931 (**7**), CCDC-976671 (**10**), CCDC-976669 (**11**), CCDC-976670 (**12**), CCDC-987539 (**13**), CCDC-976672 (**14**), and CCDC-976673 (**16**). 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) 1223/336033; e-mail, deposit@ccdc.cam-ak.uk).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, a table, and CIF files giving crystallographic data of **7**, **10−14**, and **16**, ^{1}H and ^{13}C NMR spectra (25 °C) of **1−4**, ^{1}H NMR spectra (25 °C) of compounds **6−14** and **16**, and temperature-dependent ^{1}H NMR spectra (−70 °C) of **10−12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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