Syntheses and Structures of Bisamidinate-Alane Complexes

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ABSTRACT: Insertion reactions of α,ω -biscarbodiimides (RNCN)₂X **1** - **5** (R = Et, *t*-Bu, Ph; X = C₃H₆, C₄H₈) with two equivalents of AlMe₃ yielded dinuclear tethered bisamidinate-alane complexes [RNC(Me)NAIME₂]₂X (R = Et, X = C₄H₈ **6**; R = *t*-Bu, X = C₃H₆, C₄H₈ **7**, **8**). Analogous reactions with four equivalents of AlMe₃ resulted in the coordination of two additional AlMe₃ molecules, yielding the tetranuclear bisamidinate complexes [EtN(AlMe₃)C(Me)NAIME₂]₂X (X = C₃H₆ **9**, C₄H₈ **10**) and [*t*-BuNC(Me)N(AlMe₃)AlMe₂]₂X (X = C₃H₆ **11**, C₄H₈ **12**). In addition, equimolar reactions between (RNCN)₂X (R = Et, X = C₃H₆, C₄H₈; R = Ph, X = C₄H₈) and two equivalents of AlMe₃ at elevated temperatures occurred with intramolecular cyclization and formation of [EtNC(Me)NC₃H₆N(AlMe₃)CNEt]AlMe₂ (**13**) and [RNC(Me)NC₄H₈N(AlMe₃)CNR]AlMe₂ (R = Et **14**, Ph **15**). Hydrolysis of **11** gave the protonated free ligand PhNC(Me)NC₄H₈N(H)CNPh **16** in high yield. **6** - **16** were characterized by elemental analyses, multinuclear NMR (¹H, ¹³C) and IR spectroscopy and by 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 selec-

tivity 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, ROP of lactide as well as alternating copolymerization of epoxides with CO₂.^[2]

Ligand design plays a crucial role for 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 or N,O-chelating dianionic phenoxyamido ligands as well as tridentate ligands such as tris(pyrazolyl)methanes, triazacyclohexanes, tris(imidazoles), and β -triketiminates have been established in the past for the synthesis of such multinuclear complexes.^[3,4] In addition, bisamidines of the type 1,4-C₆H₄[C{NSiMe₃}{N(SiMe₃)₂}]₂,^[5] 1,4-C₆H₄[C{NR}-{N(H)R}]₂,^[6] 1,2-[NC(Ph)N(H)R]₂C₆H₁₀ **I**,^[7] [PhN(NH*t*-Bu)C]₂ **II**^[8] and 1-[C(NR)N(H)R]-2,4-Ph₂-6-[2-[C(NR)N(H)R]C₆H₄]-C₆H₂ **III**^[9] have been used as multifunctional ligand systems and several metal complexes were reported. Moreover, CH₂-bridged [H₂C{NC(Ph)NR}]₂Li₂ **IV**,^[10] and SiMe₂-bridged bisamidinates [Me₂Si{NC(Ph)NR}]₂Li₂ **V**^[11] as well as trisamidines of type **VI**^[12] have been prepared. Very recently, we synthesized methanetrisamidines 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 ZnMe₂, AlMe₃, GaMe₃ and *i*-Bu₂AlH, respectively.^[13,15]

Scheme 1: Bis- and trisamidines as well as spacer bridged biscarbodiimides.

C_nH_{2n} -bridged α,ω -biscarbodiimides $RNCN-X_n-NCNR$ ($X_n = C_2H_4, C_3H_6, \dots$) of type **VIII** are of potential interest for the formation of tethered bimetallic bisamidinate complexes since they are more flexible compared to the CH_2 - and $SiMe_2$ -bridged systems, which is expected to be a pre-requisite for cooperative effects between two metal centers. In principle, ansa-bridged mononuclear bisamidinates might also be accessible. Early studies showed, that α,ω -bisamidinate complexes can be prepared either by reaction of α,ω -biscarbodiimides with transition metal complexes such as $CpTiMe_3$ or by reaction of a lithium salt with metal halides such as YCl_3 .^[9,16] Sita et al. reported on the use of bimetallic Zr complexes based on α,ω -bisamidinates 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 -biscarbodiimides with trimethylalane, which proceeded with formation of dinuclear tethered bisamidinate complexes via insertion of the α,ω -biscarbodiimides into the Al-Me bond of two $AlMe_3$ molecules. Reactions with four equivalents 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 -biscarbodiimides $(RNCN)_2X$ ($R = Et, X = C_3H_6$ **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 bisamidostannylenes as described by Sita et al. only gave very low yields (< 20%).^[10] We therefore decided to synthesize the α,ω -biscarbodiimides **1 - 5** by an alternate synthetic route.^[17a] In the first step, the corresponding α,ω -bisureas are synthesized (SI), which are then reacted to the α,ω -biscarbodiimides **1 - 5** (Scheme 2). Unfortunately, any attempts to obtain **5** in its pure form failed.

Scheme 2: Synthesis of **1-5**

Reactions of two equivalents of $AlMe_3$ with one equivalent of the α,ω -biscarbodiimides $(RNCN)_2X$ ($R = Et, t-Bu$; $X = C_3H_6, C_4H_8$) proceeded with insertion of the carbodiimide into the Al-Me bond and formation of the dinuclear α,ω -bisacetamidinate-alane complexes $[RNC(Me)NAIME_2]_2X$ ($R = Et, X = C_4H_8$ **6**; $R = t-Bu, X = C_3H_6$ **7**, C_4H_8 **8**, Scheme 2). The reaction of $(EtNCN)_2C_3H_6$ **1** with two equivalents 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 $[EtNC(Me)NAIME_2]_2C_3H_6$, but this compound could not be isolated in its pure form.

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 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 -bisamidinate and the bridging unit (C_3H_6, C_4H_8) clearly proved the formation of the binuclear complexes **6 - 8**.

Scheme 3: Syntheses of binuclear bisamidinate aluminum 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 two molecules in the asymmetric unit (figure 1).

Figure 1: Solid state structure of **7**. Thermal ellipsoids shown at 50% probability levels. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) 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 bisamidinate ligand in **7** acts as N,N'-chelating ligand to two AlMe_2 moieties. The average endocyclic N-C-N ($109.76(13)^\circ$) and N-Al-N ($68.84(6)^\circ$) and exocyclic C-Al-C ($116.03(8)^\circ$) 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 $\text{CC}(\text{NC})_2\text{AlC}_2$ with bond types set to "any", showing comparable endocyclic N-C-N (av.

$109.4(18)^\circ$) and N-Al-N bond angles (av. $68.9(6)^\circ$) as well as exocyclic C-Al-C (av. $118(2)^\circ$) bond angles. In addition, five binuclear bisamidinate alane complexes have been structurally characterized, to date, whose average endocyclic N-C-N (110.27°) and N-Al-N bond angles (68.70°) and exocyclic C-Al-C (117.87°) 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 number, 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 four equivalents of AlMe_3 resulted in the coordination of two additional AlMe_3 molecules, yielding the tetranuclear bisamidinate complexes $[\text{EtN}(\text{AlMe}_3)\text{C}(\text{Me})\text{NAlMe}_2]_2\text{X}$ ($\text{X} = \text{C}_3\text{H}_6$ **9**, C_4H_8 **10**) and $[\text{t-BuNC}(\text{Me})\text{N}(\text{AlMe}_3)\text{AlMe}_2]_2\text{X}$ ($\text{X} = \text{C}_3\text{H}_6$ **11**, C_4H_8 **12**), respectively. Jordan *et al.* reported on the reaction of a comparable thioamidinate alane complex $\{\text{MeC}(\text{NAd})\text{S}\}\text{AlMe}_2$ with AlMe_3 , which was shown by ^1H NMR spectroscopy to form the corresponding sulfur adduct $\{\text{MeC}(\text{NAd})\text{S}(\text{AlMe}_3)\}\text{AlMe}_2$.^[28]

Scheme 4: Syntheses of tetranuclear bisamidinate aluminum complexes **9** - **12**.

The NMR spectra of **9** - **12** showed broad resonances of the AlMe_2 moieties compared 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. Figure 2 exemplarily shows the ^1H NMR spectra recorded for **11** in the temperature range from -70°C to 25°C . The broad resonance as-observed for the AlMe_3 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 one separates upon cooling to 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 the relative intensity of 6:6:18. Comparable findings were observed for **10**, and **12**, respectively (SI).

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

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

Figure 3: Solid state structure of **10**. Thermal ellipsoids shown at 50% probability levels. Hydrogen atoms omitted for clarity. Pale colored part of the molecule generated via $1-x, 1-y, 1-z$. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) of **10**. $\text{Al}(1)\text{-N}(1)$ 1.9510(11), $\text{Al}(1)\text{-N}(2)$ 2.0077(11), $\text{Al}(2)\text{-N}(2)$ 2.0567(11), $\text{N}(1)\text{-C}(1)$ 1.2873(16), $\text{N}(1)\text{-C}(2)$ 1.4619(17), $\text{N}(2)\text{-C}(1)$ 1.4151(17), $\text{C}(1)\text{-N}(1)\text{-C}(2)$ 124.37(11), $\text{C}(1)\text{-N}(1)\text{-Al}(1)$ 93.31(8), $\text{C}(2)\text{-N}(1)\text{-Al}(1)$ 42.20(8), $\text{C}(1)\text{-N}(2)\text{-Al}(1)$ 87.18(7), $\text{C}(1)\text{-N}(2)\text{-Al}(2)$

109.30(8), $\text{Al}(1)\text{-N}(2)\text{-Al}(2)$ 113.29(5), $\text{C}(2)\text{-C}(3)\text{-C}(3)^{\#2}\text{-C}(2)^{\#2}$ 180, $\text{N}(1)\text{-C}(2)\text{-C}(3)\text{-C}(3)^{\#2}$ -179.79(14).

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 conformation of the bridging amidinate ligands is 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 centro-symmetry is not possible. The molecular structures are depicted in figures 1 – 3. The bisamidinate ion in **9** – **12** acts as N,N'-chelating ligand to the AlMe_2 moiety and also as 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° .

10, **11** and **12** show comparable endocyclic N-C-N (**10** 110.45(11); **11** 109.94(14); **12** 110.00(11) $^\circ$) and N-Al-N (**10** 68.24(4); **11** 68.65(10); **12** 68.40(4) $^\circ$) 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) $^\circ$) bond angles (average values where applicable), which are almost identical to 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 demand of the non-equal 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 those reported for the binuclear bisamidinate alane complexes.^[6,25,26]

The most surprising difference between 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 $\text{N}_{\text{amidinate}}$ atom, whereas the inner $\text{N}_{\text{amidinate}}$ atom binds to the AlMe_3 Lewis acid in **11** and **12**. Obviously, the sterically more demanding *t*-Bu group in **11** and **12** favors the coordination of the AlMe_3 molecules to the inner $\text{N}_{\text{amidinate}}$ 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 $\text{N}_{\text{amidinate}}$ atom. Moreover, the σ -coordination mode strongly influences the electron-

ic structure of the ligand, since the coordination number of the coordinating N atom increases to four, 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 significant different C–N bond lengths (**10** N(1)–C(1) 1.2873(16), N(2)–C(1) 1.4151(17); **11** N(1)–C(4) 1.425(3), N(2)–C(4) 1.290(3); **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 to this finding, the mean Al–N(sp^3) bond lengths (**10** 1.98(2); **11** 2.026(17); **12** 2.03(2) Å) are longer than the mean Al–N(sp^2) ones (**10** 1.9510(11); **11** 1.952(2); **12** 1.9501(11) Å). These findings are in remarkable contrast to those observed in the mononuclear aluminum amidinate complexes, whose N–C (av. 1.340 Å) and N–Al bond lengths (av. 1.929 Å) are very similar, indicating almost perfect π -delocalization within the amidinate backbone.

Figure 4: Solid state structure of **11**. Thermal ellipsoids shown at 50% probability levels. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) 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 shown at 50% probability levels. Hydrogen atoms omitted for clarity. Pale colored part of the molecule generated via $-x, -y, 1-z$. Selected bond lengths (Å) and angles (°) 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).

We also investigated reactions between $(\text{RNCN})_2\text{X}$ (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 $[\text{EtNC}(\text{Me})\text{NC}_3\text{H}_6\text{N}(\text{AlMe}_3)\text{CNEt}]\text{AlMe}_2$ (**13**) and $[\text{RNC}(\text{Me})\text{NC}_4\text{H}_8\text{N}(\text{AlMe}_3)\text{CNR}]\text{AlMe}_2$ (R = Et **14**, Ph **15**), respectively, rather than with formation of the *ansa-type* complexes. **13** – **15** were also prepared in higher yields by analogous reaction with two equivalents of AlMe_3 at 90 °C.

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, any 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.

Scheme 5: Syntheses of **13** - **15**.

Single crystals of **13** and **14** were obtained upon storage of solutions in hexane at $-30\text{ }^\circ\text{C}$ for 24 hours. **13** and **14** (figures 6 and 7) crystallize in the monoclinic space group $P2_1/c$ (**13**) and $P2_1/n$ (**14**). In both molecules, the AlMe_2 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 almost planar arrangement in both molecules (rms deviation from best plane; **13**: 0.1379 Å and 0.1281 Å; **14**: 0.4975 Å, C3 and C6 with approx. 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.

Figure 6: Asymmetric unit of **13**. Thermal ellipsoids shown at 50% probability levels. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) 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 shown at 50% probability levels. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$) 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).

Finally, the raw product of **15** was reacted with an excess of methanol in order to synthesize the free ligand $\text{PhNC}(\text{Me})\text{NC}_4\text{H}_8\text{N}(\text{H})\text{CNPh}$ **16**. **16** was obtained in form of X-ray quality crystals after workup in reasonable yield.

Scheme 6: Syntheses of **16**.

16 crystallizes in the monoclinic space group $P 2_1/n$ (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 $62.9(2)^\circ$). 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 $2.037 \text{ \AA}$, D-H...A 170.99°) forming a centro-symmetric $R^2_2(8)$ motif comparable to the one 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.

Figure 8: Solid state structure of **16**. Thermal ellipsoids shown at 50% probability levels. Hydrogen atoms omitted for clarity. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) 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) $113.67(14)$.

CONCLUSIONS

A series of dinuclear α,ω -bisamidinate-alane **6** – **8** complexes have been prepared by reaction of α,ω -biscarbodiimines with a twofold amount of AlMe_3 at ambient temperature. Reactions with a fourfold amount of AlMe_3 yielded tetranuclear bisamidinate complexes **9** – **12**, in which two additional AlMe_3 molecules are coordinated by either the inner or the 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 -biscarbodiimines with two equivalents 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 bisamidinate **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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to internal deuterobenzene ($\text{C}_6\text{D}_5\text{H}$, ^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$) and deuterodichloromethane (CH_2Cl_2 , ^1H : $\delta = 5.32$; CD_2Cl_2 , ^{13}C : $\delta = 53.84$). 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 -biscarbodiimides 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 bisureas, which were prepared in high yields (see SI).

(EtNCN) $_2\text{C}_3\text{H}_6$ **1**: Yield 2.10 g (43.4 %). ^1H NMR (300 MHz, C_6D_6 , 25°C): $\delta = 0.95$ (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) $_2$ C $_4$ H $_8$ 2: Yield 2.28 g (51.3 %). ^1H NMR (300 MHz, C_6D_6 , 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*-BuNCN) $_2$ C $_3$ H $_6$ 3: Yield 2.70 g (46.2 %). ^1H NMR (300 MHz, C_6D_6 , 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*-BuNCN) $_2$ C $_4$ H $_8$ 4: Yield 2.62 g (47.6 %). ^1H NMR (300 MHz, C_6D_6 , 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) $_2$ C $_4$ H $_8$ 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, CH_2Cl_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 -biscarbodiimide (**6**: 0.40 g, 1.8 mmol; **7**, **8**: 0.44 g, 1.8 mmol) in 15 mL of toluene. The solution was allowed to warm to ambient temperature within 12 h. All volatiles were evaporated in vacuum, yielding **6 - 8** as colorless

solids. Analytically pure **6 - 8** were obtained upon re-crystallization of solutions in hexane/toluene at -30 °C.

(EtNC(Me)NAlMe $_2$) $_2$ C $_4$ H $_8$ 6: Yield 0.50 g (80.3 %). Melting point: 81 °C (dec.). Anal. Found (calcd) for $\text{C}_{16}\text{H}_{36}\text{Al}_2\text{N}_4$ (338.44 g/mol): H, 10.60 (10.72); C, 56.90 (56.78). ^1H NMR (300 MHz, CH_2Cl_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*-BuNC(Me)NAlMe $_2$) $_2$ C $_3$ H $_6$ 7: Yield 0.57 g (83.2 %). Melting point: 118 °C (dec.) Anal. Found (calcd) $\text{C}_{19}\text{H}_{42}\text{Al}_2\text{N}_4$ (380.52 g/mol): H, 10.78 (11.12); C, 60.30 (59.97). ^1H NMR (300 MHz, C_6D_6 , 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*-BuNC(Me)NAlMe $_2$) $_2$ C $_4$ H $_8$ 8: Yield 0.58 g (81.7 %). Melting point: 121.4 °C (dec.). Anal. Found (calcd) for $\text{C}_{20}\text{H}_{44}\text{Al}_2\text{N}_4$ (394.55 g/mol): H, 10.9 (11.24); C, 59.00 (60.88). ^1H NMR (300 MHz, C_6D_6 , 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 -biscarbodiimide (**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 in vacuum, yielding **9 - 12** as colorless solids. Analytically pure **9 - 12** were obtained upon re-crystallization of solutions in toluene at -30 °C.

[EtN(AlMe₃)C(Me)NAlMe₂]₂C₃H₆ 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 C₂₁H₅₂Al₄N₄ (468.58 g/mol): H, 10.90 (11.18); C, 53.48 (53.82). ¹H NMR (300 MHz, C₆D₆, 25 ° C): δ = −0.27 (bs, 30 H, AlMe), 0.91 (t, 6 H, CH₂CH₃), 1.33 (bs, 8 H, CH₂, CMe), 2.77 (m, 8 H, CH₂CH₃, CH₂). ¹³C NMR (75 MHz, C₆D₆, 25 ° C): δ = −11.1 (AlMe), −7.0 (AlMe), 13.4 (CH₃), 15.9 (CH₃), 32.2 (CH₂), 41.5 (CH₂), 47.2 (CH₂), 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(AlMe₃)C(Me)NAlMe₂]₂C₄H₈ 10: Yield 0.77 g (88.6 %). Melting point: 84 ° C (dec.). Anal. Found (calcd) for C₂₂H₅₄Al₄N₄ (482.61 g/mol): H, 10.93 (11.28); C, 54.34 (54.75). ¹H NMR (300 MHz, CHDCl₂, 25 ° C): δ = −0.67 (s (br), 30 H, AlMe₂), 1.14 (t, 6 H, CH₂CH₃), 1.53 (m, 4 H, CH₂), 2.05 (s, 6 H, CMe), 3.15 (m, 4 H, CH₂CH₃), 3.18 (q, 4 H, CH₂). ¹³C NMR (75 MHz, CD₂Cl₂, 25 ° C): δ = −11.5 (AlMe), −7.6 (AlMe), 16.0 (CMe), 29.1 (CH₂), 30.4 (CH₃), 41.1 (CH₂), 46.3 (CH₂), 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(AlMe₃)C(Me)NAlMe₂]₂C₃H₆ 11: Yield 0.84 g (88.9 %). Melting point: 126.0 ° C (dec.). Anal. Found (calcd) for C₂₅H₆₀Al₄N₄ (524.69 g/mol): H, 11.33 (11.5); C, 55.97 (57.2). ¹H NMR (300 MHz, C₆D₆, 25 ° C): δ = −0.35 (s, 18 H, AlMe₃), −0.30 (s, 12 H, AlMe₂), 1.02 (s, 18 H, CMe₃), 1.59 (s, 6 H, CMe), 1.72 (quint, 2 H, CH₂CH₂CH₂), 2.87 (m, 4 H, CH₂). ¹³C NMR (75 MHz, C₆D₆, 25 ° C): δ = −9.3 (AlMe₃), −6.6 (AlMe₂), 14.8 (CMe), 31.0 (CMe₃), 32.5 (CH₂), 43.1 (CH₂), 51.1 (CMe₃), 175.7 (NCN). 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(AlMe₃)C(Me)NAlMe₂]₂C₄H₈ 12: Yield 0.87 g (89.8 %). Melting point: 127.0 ° C (dec.). Anal. Found (calcd) for C₂₆H₆₂Al₄N₄ (538.72 g/mol): H, 11.41 (11.60); C, 58.05 (57.97). ¹H NMR (300 MHz, C₆D₆, 25 ° C): δ = −0.35 (s, 18 H, AlMe₃), −0.26 (s, 12 H, AlMe₂), 1.04 (s, 18 H, CMe₃), 1.52 (m, 10 H, CH₂, CCH₃), 2.79 (m, 4 H, NCH₂). ¹³C NMR (75 MHz, C₆D₆, 25 ° C): δ = −9.1 (AlMe₃), −6.6 (AlMe₂), 15.1 (CMe), 29.4 (CH₂), 30.9 (NCMe₃), 45.6

(NCH₂), 51.4 (NCMe₃), 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 AlMe₃ 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-biscarbodiimide (**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, heated to 90 ° C and stirred for 15 min. All volatiles were evaporated in vacuum after the solution was cooled to ambient temperature, yielding **13 - 15** as colorless crystalline solids. Analytically pure **13** and **14** were obtained upon re-crystallization of solutions in hexane/toluene at −30 ° C.

[EtNC(Me)NC₃H₆N(AlMe₃)CNEt]AlMe₂ 13: Yield 0.52 g (89.0 %). Melting point: 96 ° C. (dec.). Anal. Found (calcd) for C₁₅H₃₄Al₂N₄ (324.42 g/mol): H, 10.32 (10.56); C, 55.18 (55.53). ¹H NMR (300 MHz, C₆D₆, 25 ° C): δ = −0.55 (s, 6 H, AlMe₂), −0.21 (s, 9 H, AlMe₃), 0.61 (t, 3 H, CH₂CH₃), 0.96 (s, 3 H, CMe), 1.04 (t, 3 H, CH₂CH₃), 1.62 (quint, 2 H, CH₂), 2.64 (q, 2 H, CH₂), 2.74 (t, 2 H, CH₂), 3.07 (t, 2 H, CH₂), 3.67 (q, 2 H, CH₂). ¹³C NMR (75 MHz, C₆D₆, 25 ° C): δ = −11.1 (AlMe₂), −6.7 (AlMe₂), 14.6 (CH₃), 15.7 (CH₃), 16.2 (CH₃), 41.1 (CH₂), 41.5 (CH₂), 42.9 (CH₂), 44.7 (CH₂), 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)NC₄H₈N(AlMe₃)CNEt]AlMe₂ 14: Yield 0.53 g (85.2 %). Melting point: 98 ° C (dec.). Anal. Found (calcd) for C₁₆H₃₆Al₂N₄ (338.44 g/mol): H, 10.54 (10.72); C, 56.35 (56.78). ¹H NMR (300 MHz, CHDCl₂, 25 ° C): δ = −1.00 (s, 9 H, AlMe₃), −0.83 (s, 6 H, AlMe₂), 0.92 (t, 3 H, CH₂CH₃), 1.22 (t, 3 H, CH₂CH₃), 1.76 (m, 4 H, CH₂), 2.47 (s, 3 H, CMe), 3.47 - 3.50 (m, 6 H, CH₂CH₃, CH₂). ¹³C NMR (125 MHz, CD₂Cl₂, 25 ° C): δ = −11.5 (AlMe₃), −7.0 (AlMe₂), 15.0 (CH₃), 16.2 (CH₃), 17.6 (CH₃), 27.0 (CH₂), 27.6 (CH₂), 43.0 (CH₂), 43.7 (CH₂), 49.3 (CH₂), 52.0 (CH₂), 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)NC₄H₈N(AlMe₃)CNPh]AlMe₂ 15: Any attempts to purify **15** failed. The ¹H NMR spectrum always showed additional resonances aside from those, which were addressed to **15**. ¹H NMR (300 MHz, CH₂Cl₂, 25 ° C): δ = −1.38 (s, 6 H, AlMe₃), −1.07 (s, 9 H, AlMe₂), 1.85 (m, 4 H, CH₂), 2.32 (s, 3 H, CMe), 3.30 (m, 2 H, CH₂), 3.73 (m, 2 H, CH₂), 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 stirred for 30 min. MeOH was then evaporated in vacuum, yielding a white solid, from which analytically pure **16** was isolated after extraction with CH₂Cl₂ followed by evaporation of the solvent.

PhNC(Me)NC₄H₈N(H)CNPh 16: Yield 0.14 g (48 %). Melting point: 145.5 ° C (dec.). Anal. Found (calcd) for C₁₉H₂₂N₄ (306.41 g/mol): H, 7.18 (7.24); C, 74.37 (74.48). ¹H NMR (300 MHz, CH₂Cl₂, 25 ° C): δ = 1.62 (m, 2 H, CH₂), 1.77 (m, 2 H, CH₂), 2.09 (s, 3 H, CMe), 3.28 (m, 2 H, CH₂), 3.95 (m, 2 H, CH₂), 4.77 (s, 1 H, NH), 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). ¹³C NMR (75 MHz, CD₂Cl₂, 25 ° C): δ = 17.9 (CMe₃), 27.1 (CH₂), 29.5 (CH₂), 44.1 (CH₂), 45.7 (CH₂), 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 (MoKα radiation, λ = 0.71073 Å) at low temperatures are summarized in Table 1. The solid-state structures of **7**, **10** – **14** and **16** are shown in Figures 1 and 3 - 8. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97).^[32,33] **14** was a pseudo-merohedral twin and was refined accordingly. The major component comprised approx. 90%. Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (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 CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam-ac.uk).

ASSOCIATED CONTENT

Supporting Information

Electronic Supplementary Information (ESI) available: Cif files of **7**, **10** – **14** and **16**. In addition, ¹H and ¹³C NMR spectra (25 ° C) of **1** - **4**, ¹H NMR spectra (25 ° C) of compounds **6** - **14** and **16** as well as temperature-dependent ¹H NMR spectra (-70 ° C) of **10** - **12** are shown in the SI. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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A series of dinuclear and tetranuclear α,ω -bisamidinate-alane complexes have been prepared by reaction of dinuclear α,ω -biscarbodiimines with various amounts of AlMe_3 at different temperatures.

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