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Synthesis, structure, and catalytic activity of dinuclear aluminium bis(amidinate) and bis(guanidinate) complexes†

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Eight dinuclear methyl aluminium(III) bis(amidinate) and bis(guanidinate) complexes have been synthesized in good to very good yields and were fully characterized by means of ¹H, ¹³C, and IR spectroscopy as well as elemental analysis. Five of them were successfully converted to the respective dinuclear aluminium iodide complexes and a dinuclear aluminium chloride bis(amidinate) complex was directly accessed by deprotonation of the ligand using ethyl aluminium dichloride. The molecular solid-state structures of eleven complexes were obtained from X-ray diffraction analysis. Furthermore, the catalytic activity of the dinuclear methyl aluminium complexes **3** and **4** has been probed in the ring-opening polymerization of ε-caprolactone and L-lactide and the results highlight the impact of the metal–metal separation and the ligands' backbone on activity and selectivity.

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Introduction

The previous decades have seen a remarkable development of new catalytic methods associated with increased reactivity and selectivity schemes, while using less toxic, abundant, and non-endangered elements instead of scarce and correspondingly expensive noble metals.¹ Among the various concepts, cooperative catalysis is one of the most versatile and powerful approaches, and dinuclear or bimetallic compounds often excel the related single-site homogeneous catalysts.² Reactivity and selectivity patterns can be controlled by designing tailor-made ditopic ligands, which allow modifying the metal–metal separation, the relative orientation of both active sites and also the steric constraints of the dinuclear catalyst. Ditopic ligands possessing two monoanionic *N,N'*-binding pockets have been regularly utilized for the complexation of non-precious metals,³ and bis(amidinate)s⁴ received considerable interest in the past. The use of the more electron-rich bis(guanidine)s,⁵ however,

has only recently started to evolve, likely due to the higher synthetic demands. In both cases, the two binding sites can be connected through either one or two of the chelating nitrogen atoms, affording acyclic and macrocyclic ligands, respectively, or through the ligands' backbone, Fig. 1.⁶

The ligand framework affects the overall orientation of the two metal sides and allows for or impedes cooperative effects as illustrated in various applications of the related polynuclear complexes in material science and catalysis.^{6a,7a–i} However, examples incorporating p-block elements remain rare,^{3,4e,j,l,m,n,o,p,y,7h,8} and only a few reports about dinuclear aluminium bis(amidinate) complexes exist in the literature.^{7g,h,8c} In terms of catalysis, dinuclear aluminium bis(amidinate)s have been applied for the fixation of carbon dioxide into cyclic carbonates^{7h} and for the ring-opening polymerization (ROP) of cyclic esters including ε-caprolactone and L-lactide.^{7g,8c} With respect to the latter, cooperative effects were not observed in case of the backbone-bridged bis(amidinate)s,^{8c} likely because of the opposing orientation of the two active sites, while in case of the nitrogen-bridged relatives cooperativity was seen.^{7g} However, only two aromatic bridging groups have been studied and experiments in which

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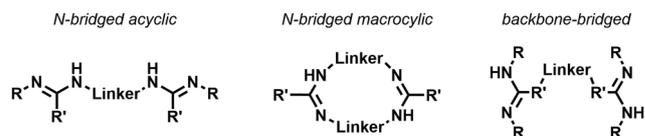
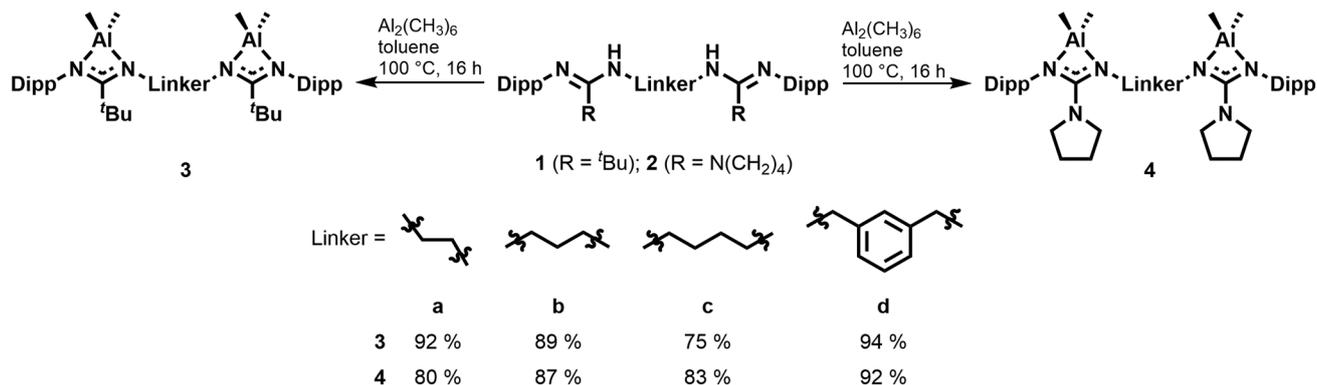


Fig. 1 Various types of bis(amidinate)s (*R'* = alkyl, aryl) and bis(guanidinate)s (*R'* = *NR''R'''*).



Scheme 1 Synthesis of the dinuclear methyl aluminium bis(amidinate) **3** and bis(guanidinate) **4** complexes from the respective protio-ligands by methane elimination. Dipp = 2,6-diisopropylphenyl.

the metal–metal separation is systematically altered have yet to be performed. This is somewhat surprising as dinuclear alkyl aluminium complexes based on various ditopic ligands have been identified as powerful catalysts in the ring-opening polymerization of polar monomers.^{7f,i,9} Hence, we set out to synthesize new dinuclear aluminium alkyl complexes, which possess more flexible ethylene, propylene, butylene, and 1,3-xylylene bridging groups. Aiming to elucidate the impact of the ligands' backbone without influencing the steric demand significantly, bis(guanidinate) complexes have been synthesized and investigated as well and our findings are reported in the following.

Results and discussion

Synthesis and structural characterization of dinuclear aluminium complexes

The dinuclear aluminium bis(amidinate) and bis(guanidinate) complexes **3** and **4** were obtained from the related protio-ligands, which have been synthesized according to reported procedures,^{4a,e,5d,10} using protocols established for dinuclear alkyl aluminium bis(β -diketiminate) complexes.¹¹ Hence, toluene solutions of **1** or **2** were allowed to react with trimethyl aluminium at 100 °C overnight, Scheme 1, affording the respective complexes **3** and **4** in good to very good yields as colourless, partially crystalline powders using a simple work-up procedure. The complexes **3** and **4** have been characterized by elemental analyses, ¹H and ¹³C NMR as well as IR spectroscopy. Notably, ²⁷Al NMR resonances could not be detected despite extended numbers of scans; most likely, this is caused by the low symmetry of the aluminium centers, which causes considerable line-broadening due to quadrupolar interactions.¹² Common features observed in the respective ¹H NMR spectra include one singlet for the aluminium methyl groups (δ between -0.90 and -0.21 ppm) as well as one septet and two doublets for iso-propyl groups of the 2,6-diisopropylphenyl substituent, a pattern consistent with conformational averaging on the NMR time scale at room temperature.

Furthermore, we were able to obtain single crystals suitable for an X-ray diffraction analysis of the species **3a**, **3c**, and **4a-c** and their molecular structures in the solid state are shown in Fig. 2 and 3. The Al–C bond lengths with values in between 1.9507(14) and 1.9692(16) Å are comparable to those reported

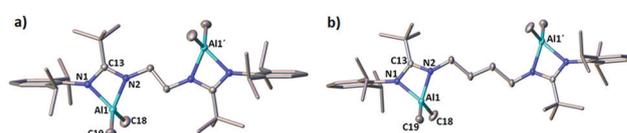


Fig. 2 Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of: (a) **3a**: Al1–Al1' 6.2911(7), Al1–C18 1.9580(14), Al1–C19 1.9507(14), Al1–N1 1.9441(10), Al1–N2 1.915(1), N1–C13 1.3479(15), N2–C13 1.3379(15), N1–Al1–N2 68.27(4), N1–C13–N2 107.47(9), C18–Al1–C19 117.18(6); (b) **3c**: Al1–Al1' 8.1793(6), Al1–C18 1.9599(14), Al1–C19 1.9589(13), Al1–N1 1.9358(9), Al1–N2 1.9196(10), N1–C13 1.3449(14), N2–C13 1.3396(14), N1–Al1–N2 68.41(4), N1–C13–N2 107.68(9), C18–Al1–C19 117.56(6).

for other methyl aluminium amidinate (1.937(6) and 1.958(3) Å),¹³ guanidinate (1.955(4) and 1.9726(19) Å),¹⁴ bis(amidinate) (1.943(4) and 1.946(4) Å),^{4f} and bis(guanidinate) complexes (1.925(7) and 1.962(3) Å).¹⁵ The same holds true for the Al–N bond lengths (1.915(1) to 1.9441(10) Å) and N–Al–N bite angles (68.27(4) to 69.89(5)°). Although small differences in the C–N bond lengths were observed between the bis(amidinate)s (1.3379(15) to 1.3479(15) Å) and bis(guanidinate)s (1.3421(18) to 1.3704(17) Å), the values indicate effective electron delocalization throughout the N–C–N backbone in both cases. The aluminium-aluminium separation in the solid state increases proportional to the number of carbon atoms in the linker moiety ranging from 6.2911(7) Å (**3a**) to 8.2085(6) Å (**4c**).

Due to our interest in Group 13 analogues of bis(carbene)s¹⁶ we intended to convert the dinuclear methyl aluminium bis(amidinate) and bis(guanidinate) complexes **3** and **4** by iodization using elemental iodide to the related dinuclear aluminium iodide complexes **5** and **6**. While bis(amidinate) complexes **5** could be obtained in acceptable to good yields, **6b** was the only bis(guanidinate) complex that we were able to isolate although only in poor yield, Scheme 2. Possible side reactions of the strongly-basic and nucleophilic ligand framework with electrophilic methyl iodide formed during the reaction may account for this. Attempts to follow this side reaction by ¹H NMR were not successful and gave complex spectra with broadened and overlapping resonances.

Besides the absence of the Al(CH₃)₂ resonances, the room-temperature ¹H NMR spectra resemble by and large those of the

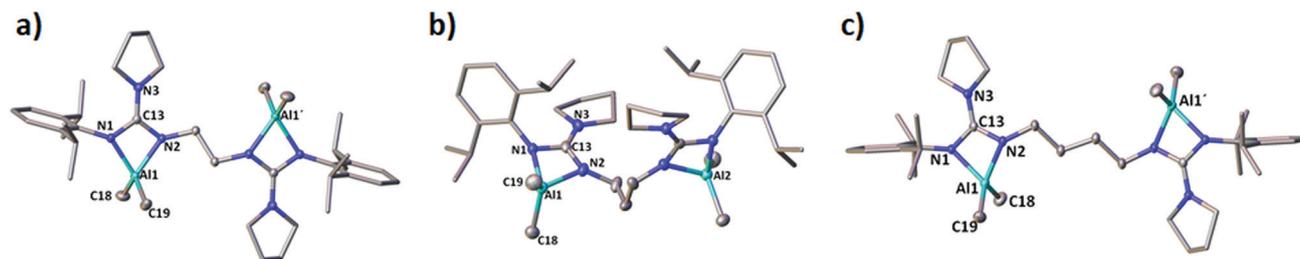
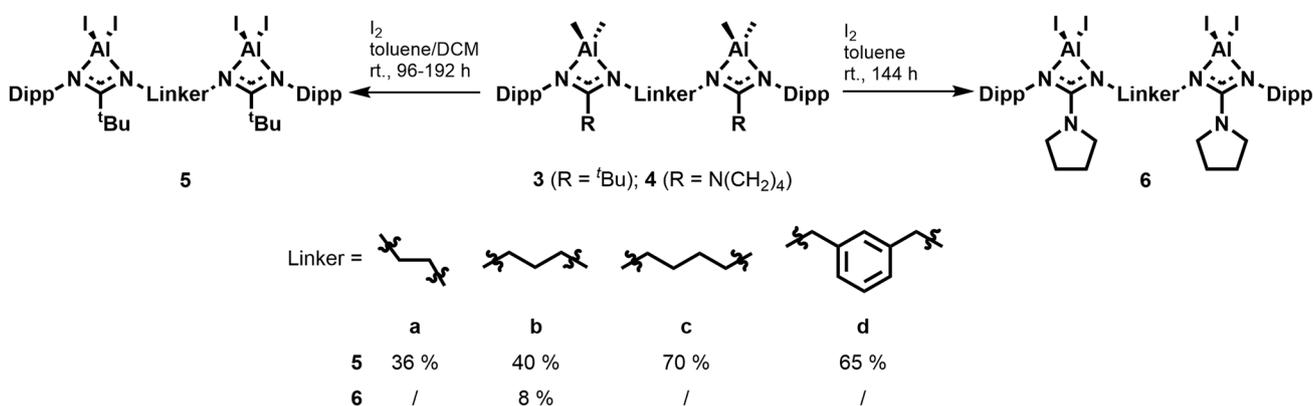


Fig. 3 Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of: (a) **4a**: Al1–Al1' 6.3264(9), Al1–C18 1.9651(16), Al1–C19 1.9653(14), Al1–N1 1.9339(11), Al1–N2 1.9203(11), N1–C13 1.3543(16), N2–C13 1.3489(16), N3–C13 1.3484(16), N1–Al1–N2 69.54(5), N1–C13–N2 108.8(1), N1–C13–N3 125.87(11), N2–C13–N3 125.33(11), C18–Al1–C19 118.19(7); (b) **4b**: Al1–Al2 6.5520(6), Al1–C18 1.9691(16), Al1–C19 1.9553(17), Al1–N1 1.9271(13), Al1–N2 1.9196(13), N1–C13 1.3704(17), N2–C13 1.3421(18), N3–C13 1.3439(17), N1–Al1–N2 69.89(5), N1–C13–N2 108.64(11), N1–C13–N3 122.84(12), N2–C13–N3 128.50(13), C18–Al1–C19 117.70(7); (c) **4c**: Al1–Al1' 8.2085(6), Al1–C18 1.9561(14), Al1–C19 1.9645(14), Al1–N1 1.929(1), Al1–N2 1.919(1), N1–C13 1.3549(15), N2–C13 1.3466(15), N3–C13 1.3441(15), N1–Al1–N2 69.69(4), N1–C13–N2 108.94(10), N1–C13–N3 124.93(10), N2–C13–N3 126.11(10), C18–Al1–C19 116.17(6).



Scheme 2 Synthesis of the dinuclear aluminium iodide complexes **5** and **6** from the respective alkyl aluminium bis(amidinate) and bis(guanidinate) complexes. Dipp = 2,6-diisopropylphenyl.

dinuclear methyl aluminium complexes **3** and **4** and the simple set of resonances associated with the 2,6-diisopropylphenyl groups indicates a symmetric or averaged structure in solution. In agreement with previous reports on dinuclear aluminium iodide complexes,^{17–27} ²⁷Al NMR resonances could not be detected. In addition to the full characterization by elemental analyses, ¹H and ¹³C NMR as well as IR spectroscopy, we were able to isolate single-crystals suitable for X-ray diffraction analysis of the complexes **5a–d**, and **6b**. Their molecular structures in the solid state are shown in Fig. 4 and 5a.

The aluminium–iodine bond lengths of the bis(amidinate) complexes **5a–5d** (2.4752(15) to 2.523(2) Å) are slightly longer compared to their mononuclear relatives (2.438(3) and 2.481(3) Å).¹⁸ In case of the bis(guanidinate) complex **6b** the Al–I distances (2.5027(6) and 2.5076(6) Å) resemble values of the respective guanidinate complexes (2.5029(19) to 2.5169(16) Å),¹⁹ but are slightly longer as compared to the only other yet reported dinuclear bis(guanidinate) aluminium iodide complex (2.4555(18) and 2.477(2) Å).¹⁵ By substituting the methyl for the iodo rests, the Al–N bond lengths of **5a–5d** (1.868(4) to 1.896(3) Å) and **6b** (1.8703(16) and 1.8757(2) Å) are shortened due to the increased polarization and match by and large reported values of

related amidinate (Al–N 1.884(7) and 1.889(8) Å) and guanidinate complexes (Al–N 1.886(5) and 1.896(5) Å). In consequence, the N–Al–N bite angles of **5a–5d** (70.21(17) to 71.2(2)°) and **6b** (72.21(7)°) are more obtuse. The Al–Al distances, finally, are only slightly longer than those of **3** and **4**. In direct comparison of **5c** and **5d**, twisting in case of the latter causes a significant shorter Al–Al separation of 6.903(2) Å relative to 8.1977(14) Å for the former.

We finally wondered if dinuclear aluminium halide complexes are also directly available from the protio-ligand. Indeed, reacting the bis(amidine) **1d** with ethyl aluminium dichloride gives rise to the dinuclear aluminium chloride complex **7d** by elimination of ethane in almost quantitative yields, Scheme 3. It readily crystallizes from toluene and its solid-state structure is given in Fig. 5b. The Al–Cl (2.0981(6) and 2.1143(5) Å) and Al–N bond lengths (1.8667(13) and 1.9001(10) Å) as well as the N–Al–N bite angles (70.28(5) and 70.59(5)°) are similar to those reported for amidinate aluminium chloride complexes (Al–Cl 2.1018(14) to 2.1036(14) Å, Al–N 1.863(3) to 1.872(3) Å, N–Al–N 70.91°).^{13a} The Al–Al distance amounts to 7.4043(5) Å and is thus about 0.5 Å longer compared to **5d**.

Attempts to obtain dinuclear aluminium(i) complexes by reducing the dinuclear complexes **5c**, **5d** and **7d** using either

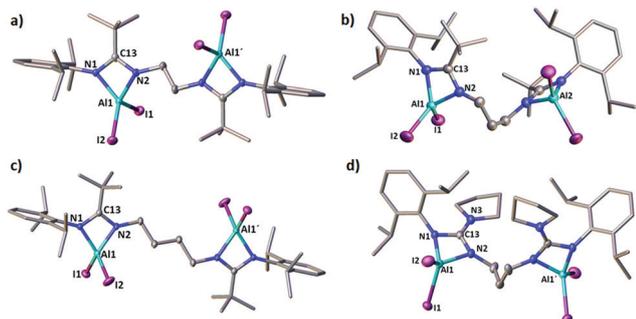


Fig. 4 Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of: (a) **5a**: Al1–Al1' 6.3599(16), Al1–I1 2.4902(12), Al1–I2 2.5005(8), Al1–N1 1.892(3), Al1–N2 1.872(3), N1–C13 1.356(4), N2–C13 1.339(4), N1–Al1–N2 70.55(11), N1–C13–N2 107.6(3), I1–Al1–I2 113.85(4); (b) **5b**: Al1–Al2 6.4993(18), Al1–I1 2.4800(12), Al1–I2 2.5037(9), Al1–N1 1.896(3), Al1–N2 1.880(3), N1–C13 1.347(5), N2–C13 1.349(4), N1–Al1–N2 70.71(14), N1–C13–N2 108.3(3), I1–Al1–I2 112.07(4); (c) **5c**: Al1–Al1' 8.1977(14), Al1–I1 2.4925(8), Al1–I2 2.4816(7), Al1–N1 1.894(2), Al1–N2 1.869(2), N1–C13 1.350(3), N2–C13 1.346(3), N1–Al1–N2 70.60(9), N1–C13–N2 107.5(2), I1–Al1–I2 112.22(3); (d) **5b**: Al1–Al1' 6.5975(10), Al1–I1 2.5076(6), Al1–I2 2.5027(6), Al1–N1 1.8703(16), Al1–N2 1.8757(17), N1–C13 1.369(2), N2–C13 1.356(2), N3–C13 1.334(2), N1–Al1–N2 72.21(7), N1–C13–N2 108.19(15), N1–C13–N3 124.24(16), N2–C13–N3 127.56(17), I1–Al1–I2 110.16(2).

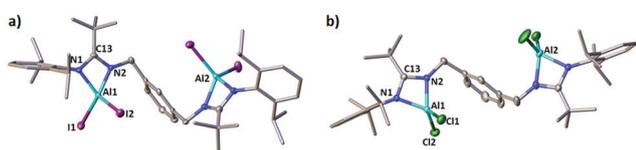
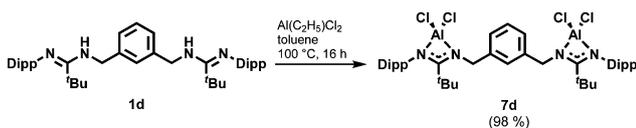


Fig. 5 Solid-state structure (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°] of: (a) **5d**: Al1–Al2 6.903(2), Al1–I1 2.4752(15), Al1–I2 2.5209(14), Al1–N1 1.895(6), Al1–N2 1.875(4), N1–C13 1.354(7), N2–C13 1.350(8), N1–Al1–N2 71.2(2), N1–C13–N2 108.4(5), I1–Al1–I2 111.22(6); (b) **7d**: Al1–Al2 7.4043(5), Al1–Cl1 2.0981(6), Al1–Cl2 2.0987(6), Al1–N1 1.8860(12), Al1–N2 1.8673(13), N1–C13 1.3456(17), N2–C13 1.3474(17), N1–Al1–N2 70.59(5), N1–C13–N2 107.28(12), Cl1–Al1–Cl2 112.79(3).



Scheme 3 Synthesis of the dinuclear aluminium bis(amidinate) chloride complex **7d** by ethane elimination. Dipp = 2,6-diisopropylphenyl.

magnesium powder, cobaltocene or potassium mirror remained unsuccessful. As very low reduction potential have been reported for dinuclear aluminium bis(β -diketiminate) halide complexes,¹⁷ we performed cyclic voltammetry experiments with the complexes **5a–d** and **6b**. Irreversible reduction events with potentials (referenced to the Fc/Fc⁺ redox couple) between -3.20 and -3.25 V, which are even lower than those of $[\{\text{CH}(\text{CMeNDipp})_2\}\text{AlI}_2]$ (-3.16 V),¹⁷ were observed for the bis(amidinate) complexes, Fig. S1–S6 (ESI[†]). Among the

alkylene-bridged complexes **5a–c**, no significant impact of the linker group was observed while in case of the 1,3-xylylene-bridged complex **5d** no reduction event was observed above -3.5 V. However, the impact of the backbone is well illustrated by comparing **5b** (-3.25 V) and **6b** (-3.07 V). Notably, the estimated value of potassium in THF amounts to -3.24 V, which may explain the unsuccessful reduction experiments.

Ring-opening polymerization of ϵ -caprolactone and L-lactide

The dinuclear methyl aluminium complexes **3** and **4** have been tested as initiators for the ring-opening polymerization of L-lactide (LLA) and ϵ -caprolactone (ϵ CL). While alcohols are regularly used as activators of dinuclear alkylaluminium complexes,^{6a,7f,i} previous reports on mononuclear dialkyl aluminium amidinate complexes mention a rapid alcoholysis.^{13b} Hence, we first probed the stability of the four-membered AlCN₂-metallacycles towards protonolysis. Adding one or two equivalents of benzyl alcohol to the complexes **3b** and **4b**, respectively, Fig. 6, affords the related protio-ligands and predominantly dimethyl aluminium benzyloxyate as evidenced by the distinct ¹H NMR shifts, Fig. S70–S75 (ESI[†]).²⁰ In consequence, and in agreement with previous reports on dialkyl aluminium amidinate complexes,^{13b} Me₂Al(OR) (R = benzyl) is formed and the complexes **3** and **4** serve only as alkyl aluminium precursors. Most likely, this behaviour is due to the less stable four-membered chelate ring in contrast to its five- and six-membered relatives.

In previous reports, dinuclear aluminium alkyl amidinate complexes have been successfully applied for the ROP of ϵ -caprolactone and L-lactide with and without the addition of an activator under various conditions.^{7g} Aiming to test the catalytic performance of the complexes **3** and **4**, we adopted the experimental conditions and the results for ϵ -caprolactone and L-lactide are subsequently discussed in the following. ϵ -caprolactone was polymerized at 70 °C in toluene for eight hours using a catalyst–monomer ratio of 1 : 200 and a monomer concentration of 1.4 mol L⁻¹, Table 1. Based on the obtained material, conversions ranging from 75 to 90% are recognized and higher values are associated with the bis(amidinate)s **3** in direct comparison with their bis(guanidinate) relatives **4**. The size-exclusion chromatography (SEC) traces, Fig. S92–S99 (ESI[†]), possess multimodal distributions showing predominantly

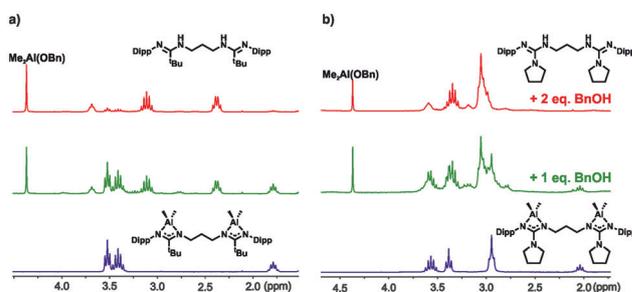


Fig. 6 Excerpts of the ¹H NMR spectra of (a) **3b** and (b) **4b** in C₆D₆ before (blue) and after the addition of one (green) and two (red) equivalents of benzyl alcohol, respectively.

Table 1 ROP of ϵ -caprolactone catalysed by the dinuclear complexes **3** and **4**. Reaction conditions: toluene 2.1 mL, 8h, 70 °C, catalyst–monomer ratio = 1 : 200, [catalyst] = 7×10^{-3} mol L⁻¹, [monomer] = 1.4 mol L⁻¹. SEC data are relative to polystyrene standard in THF and refer to the fraction with a molar mass > 2000 Da

Entry	Cat.	Conv. (%)	M_n calc ^a (g mol ⁻¹)	M_n SEC (g mol ⁻¹)	D SEC (M_w/M_n)
1	3a	82	9.36×10^3	2.88×10^3	16.68
2	3b	90	1.03×10^4	3.67×10^3	12.50
3	3c	89	1.02×10^4	6.93×10^3	12.45
4	3d	88	1.00×10^4	6.06×10^3	9.56
5	4a	78	8.90×10^3	6.94×10^3	5.91
6	4b	81	9.25×10^3	6.14×10^3	5.96
7	4c	75	8.56×10^3	6.02×10^3	5.67
8	4d	81	9.25×10^3	6.36×10^3	6.26

^a Calculated M_n = [monomer/Al] \times (conversion/100) \times MW ϵ CL.

polymeric but also oligomeric products. A number average molar mass M_n between 17.000 and 23.400 Da and rather large polydispersities D ranging from 2.07 to 2.39 were obtained when analysing the polymeric peak above 2000 Da. Overall, the bis(amidinate)s **3** give rise to higher M_n values and except of **3d** also to smaller polydispersity indices (PDIs). Notably, using **3c** affords the polymer with the lowest PDI and the highest molecular weight M_n . When comparing **3** and **4**, no distinct trend with respect to the linker length can be recognized but within each subset differences are observed. For the bis(amidinate)s **3**, the bridges containing more than two carbon atoms give rise to higher conversions than **3a**. Furthermore, the number average molar mass of the polycaprolactone (PCL) obtained by using the 1,4-butylene and 1,3-xylylene-bridged complexes **3c** and **3d** are significantly higher compared to the catalysts containing smaller bridges. In contrast, the impact of the linker on conversion and product properties is only marginal in case of the bis(guanidinate)s **4**. In comparison with previous reports,^{7g} both **3** and **4** afford products with broader dispersities and smaller M_n values.

The ring-opening polymerization of L-lactide was performed in toluene (monomer concentration of 2.0 mol L⁻¹) at 80 and 90 °C using a catalyst–monomer ratio of 1 : 200, Table 2. After 25 hours, the reactions were quenched and the products analysed by ¹H NMR spectroscopy and SEC. Increased conversions and yields were observed for the reactions at 90 °C as compared to those at 80 °C and catalysts **3b** and **4c** were found

to be best within their complex class. The increased conversion also affected the thus obtained poly-L-lactide (PLLA) and higher molecular weights were hence observed at 90 °C. In most of the cases, the experimental molecular weights are in good agreement with the calculated values for one polymer chain growing per metal centre. However, the molecular weights of the polymers obtained using **3b**, **3c** or **4b** at 80 °C as well as **3b**, **4b** or **4d** at 90 °C are 1.3 to 1.8 times higher than the calculated values for one polymer chain per metal centre suggesting a concerted chain propagation. Except the case of **3b**, the increased conversions at 90 °C come along with larger polydispersity indices ranging from 1.35 to 2.31. More pronounced back-biting and transesterification reactions are likely to account for the broader molecular weight distributions. The experimental findings illustrate well the crucial impact of both, the bridging group and the ligands' backbone. At 90 °C, the bis(guanidinate)s **4** gave rise to polymers with higher polydispersities as compared to the related bis(amidinate)s **3**. With respect to the linker length, the propylene-bridged complexes **3b** and **4b**, afforded products with the highest number average molar mass, while the most narrow polydispersity indices among each compound class are associated with the ethylene-bridged bis(amidinate) **3a** (1.35) and the propylene-bridged bis(guanidinate) **4b** (2.17). Notably, an increase of the PDI with enlarging the linker length has previously reported for bimetallic salen aluminium complexes.^{7f} However, the data reported in here do not allow deducing a general trend.

Experimental

General considerations

All preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line techniques, while the samples for analytics were handled in a glovebox (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were successively removed from the inert gas by passing it over a BASF R 3-11 (CuO/MgSiO₃) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P₄O₁₀. Dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS-800). Benzene-d₆ and toluene were used as

Table 2 ROP of L-lactide catalysed by the dinuclear complexes **3** and **4**. Reaction conditions: toluene 1.5 mL, 25 h, catalyst–monomer ratio = 1 : 200, [catalyst] = 1×10^{-2} mol L⁻¹, [monomer] = 2.0 mol L⁻¹. SEC data are relative to polystyrene standard in THF

Entry	Cat.	Temp. (°C)	Conv. ^a (%)	Yield	M_n calc ^b (g mol ⁻¹)	M_n SEC ^b (g mol ⁻¹)	D SEC (M_w/M_n)	Entry	Cat.	Temp. (°C)	Conv. ^a (%)	Yield	M_n calc ^b (g mol ⁻¹)	M_n SEC ^b (g mol ⁻¹)	D SEC (M_w/M_n)
1	3a	80	35	25	5.04×10^3	5.27×10^3	1.18	9	4a	80	45	41	6.49×10^3	7.94×10^3	2.08
2	3a	90	83	83	1.20×10^4	1.35×10^4	1.35	10	4a	90	84	79	1.21×10^4	1.29×10^4	2.22
3	3b	80	35	29	5.04×10^3	8.09×10^3	1.66	11	4b	80	40	35	5.77×10^3	1.02×10^4	1.48
4	3b	90	92	88	1.33×10^4	1.78×10^4	1.58	12	4b	90	83	80	1.20×10^4	2.12×10^4	2.15
5	3c	80	39	35	5.62×10^3	9.02×10^3	1.43	13	4c	80	48	37	6.92×10^3	8.61×10^3	1.53
6	3c	90	90	88	1.30×10^4	1.41×10^4	1.80	14	4c	90	86	80	1.24×10^4	1.33×10^4	2.31
7	3d	80	36	24	5.19×10^3	4.94×10^3	1.17	15	4d	80	24	11	3.46×10^3	8.49×10^3	1.35
8	3d	90	86	83	1.24×10^4	9.34×10^3	1.59	16	4d	90	68	62	9.80×10^3	1.43×10^4	2.17

^a Determined by ¹H NMR spectroscopy. ^b Calculated M_n = [monomer/Al] \times (conversion/100) \times MW L-lactide.

p.a. grade and were distilled from Na/benzophenone prior to use. CDCl_3 was dried by distillation from calcium hydride. Pyrrolidine, lead(II) oxide, pivaloylchloride, PCl_5 , 1,2-ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,3(aminomethyl)benzylamine, 2,6-diisopropylaniline, trimethylaluminium (2 M in toluene), iodine and ethylaluminium dichloride (1.8 M in toluene) were purchased from Sigma-Aldrich. The bis(amidines) (**1a**, **1b**, **1c**)^{4ae} as well as the bis(guanidines) (**2a**, **2b**, **2c**, **2d**)^{4ae,5d,10} were prepared according to published procedures. Further information are given in the ESI.†

Characterization

The NMR spectra were recorded with Bruker Avance 300 and 400 spectrometers ($T = 300 \text{ K}$) with δ referenced to external tetramethylsilane (^1H and ^{13}C) and aluminium(III) nitrate (^{27}Al). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak (CHCl_3 : $\delta(^1\text{H}) = 7.26$) or (C_6D_6 : $\delta(^1\text{H}) = 7.16$) and the solvent peak (CDCl_3 : $\delta(^{13}\text{C}) = 77.16$) or (C_6D_6 : $\delta(^{13}\text{C}) = 128.06$), respectively. ^{27}Al NMR spectra were calibrated relative to external $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Notably, the broad resonance at about 60 ppm is a background signal associated with the probe. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit. Elemental analysis was performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^1H NMR spectroscopy. NMR and IR spectra are given in the ESI,† Fig. S8–S70.

3a: A solution of trimethylaluminium (3.84 mL, 7.68 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **1a** (2.00 g, 3.66 mmol) in toluene (15 mL) at rt, followed by stirring at 100°C overnight. After slowly cooling to rt colourless crystals grew from the solution, which were separated and further washed with pentane ($3 \times 10 \text{ mL}$) to obtain **3a** (2.22 g, 3.37 mmol, 92%) as a white crystalline solid. ^1H NMR (400 MHz, C_6D_6): δ (ppm) = -0.21 (s, 12H, $\text{Al}(\text{CH}_3)_2$), 1.05 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.22–1.25 (m, 24H, $\text{CH}(\text{CH}_3)_2$), 3.41 (sept, $^3J_{\text{HH}} = 6.8 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 3.86 (s, 4H, CH_2CH_2), 7.00–7.10 (m, 6H, C_6H_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ (ppm) = -9.1 ($\text{Al}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$), 26.3 ($\text{CH}(\text{CH}_3)_2$), 28.3 ($\text{CH}(\text{CH}_3)_2$), 28.5 ($\text{C}(\text{CH}_3)_3$), 40.0 ($\text{C}(\text{CH}_3)_3$), 48.9 (CH_2CH_2), 123.8 ($m\text{-C}_6\text{H}_3$), 125.9 ($p\text{-C}_6\text{H}_3$), 140.0 ($o\text{-C}_6\text{H}_3$), 144.3 ($i\text{-C}_6\text{H}_3$), 180.4 ($\text{NC}(\text{C}(\text{CH}_3)_3\text{N})$); ^{27}Al NMR (104 MHz, C_6D_6): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2957 (m), 2928 (w), 2869 (w), 1412 (s), 1298 (s), 1186 (s), 773 (s), 720 (s), 673 (s); anal. calc. (found) for $[\text{C}_{40}\text{H}_{68}\text{N}_4\text{Al}_2]$: C 73.76 (73.47), H 10.32 (10.02), N 8.11 (8.35).

3b: A solution of trimethylaluminium (15.0 mL, 30.0 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **1b** (8.42 g, 15.0 mmol) in toluene (60 mL) at rt, followed by stirring at 100°C overnight. After slowly cooling to rt a crystalline solid precipitated, which was separated and further washed with hexane ($3 \times 10 \text{ mL}$). A second crop of crystals was obtained by concentration of the mother solution followed by cooling to -20°C . Repeated washing with toluene gave **3b** (9.05 g, 13.4 mmol, 89%) as a white crystalline solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = -0.66 (s, 12H, $\text{Al}(\text{CH}_3)_2$), 1.14 (d, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.17 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.27 (d, $^3J_{\text{HH}} = 6.7 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.84 (quint, $^3J_{\text{HH}} = 6.3 \text{ Hz}$, 2H, $\text{CH}_2(\text{CH}_2)\text{CH}_2$), 3.25

(sept, $^3J_{\text{HH}} = 6.8 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 3.65 (t, $^3J_{\text{HH}} = 6.4 \text{ Hz}$, 4H, $\text{CH}_2(\text{CH}_2)\text{CH}_2$), 7.04–7.13 (m, 6H, C_6H_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ (ppm) = -9.7 ($\text{Al}(\text{CH}_3)_2$), 23.3 ($\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{CH}(\text{CH}_3)_2$), 28.0 ($\text{CH}(\text{CH}_3)_2$), 28.7 ($\text{C}(\text{CH}_3)_3$), 34.1 ($\text{CH}_2(\text{CH}_2)\text{CH}_2$), 39.9 ($\text{C}(\text{CH}_3)_3$), 43.5 ($\text{CH}_2(\text{CH}_2)\text{CH}_2$), 123.4 ($m\text{-C}_6\text{H}_3$), 125.0 ($p\text{-C}_6\text{H}_3$), 140.2 ($o\text{-C}_6\text{H}_3$), 144.2 ($i\text{-C}_6\text{H}_3$), 180.2 ($\text{NC}(\text{C}(\text{CH}_3)_3\text{N})$); ^{27}Al NMR (104 MHz, CDCl_3): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2927 (vw), 2873 (w), 1416 (s), 1335 (m), 1191 (m), 775 (m), 729 (m), 669 (s); anal. calc. (found) for $[\text{C}_{41}\text{H}_{70}\text{N}_4\text{Al}_2]$: C 73.43 (73.39), H 10.56 (10.55), N 8.16 (8.26).

3c: A solution of trimethylaluminium (2.00 mL, 4.0 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **1c** (1.15 g, 2.0 mmol) in toluene (20 mL) at rt, followed by stirring at 100°C overnight. The product crystallized upon slow cooling to rt over 1 h. After solvent filtration the white crystalline powder was washed with toluene ($2 \times 5 \text{ mL}$) to afford **3c** (1.04 g, 1.5 mmol, 75%) as a white crystalline powder. ^1H NMR (300 MHz, CDCl_3): δ (ppm) = -0.69 (s, 12H, $\text{Al}(\text{CH}_3)_2$), 1.12–1.16 (m, 30 H, $\text{C}(\text{CH}_3)_3$, $\text{CH}(\text{CH}_3)_2$), 1.26–1.29 (m, 12H, $\text{CH}(\text{CH}_3)_2$), 1.66 (quint, $^3J_{\text{HH}} = 3.3 \text{ Hz}$, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 3.27 (sept, $^3J_{\text{HH}} = 6.9 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 3.53 (t, $^3J_{\text{HH}} = 6.0 \text{ Hz}$, 4H, $\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 7.03–7.20 (m, 6H, C_6H_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ (ppm) = -9.7 ($\text{Al}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$), 26.2 ($\text{CH}(\text{CH}_3)_2$), 28.0 ($\text{C}(\text{CH}_3)_3$), 28.8 ($\text{CH}(\text{CH}_3)_2$), 30.2 ($\text{C}(\text{CH}_3)_3$), 39.8 ($\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 46.6 ($\text{CH}_2(\text{CH}_2)_2\text{CH}_2$), 123.4 ($m\text{-C}_6\text{H}_3$), 125.0 ($p\text{-C}_6\text{H}_3$), 140.3 ($o\text{-C}_6\text{H}_3$), 144.4 ($i\text{-C}_6\text{H}_3$), 179.6 ($\text{NC}(\text{C}(\text{CH}_3)_3\text{N})$); ^{27}Al NMR (104 MHz, CDCl_3): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (m), 2939 (w), 2872 (w), 1419 (s), 1351 (s), 1188 (m), 774 (m), 727 (m), 670 (s); anal. calc. (found) for $[\text{C}_{42}\text{H}_{72}\text{N}_4\text{Al}_2]$: C 73.17 (73.38), H 10.48 (10.25), N 8.33 (8.09).

3d: A solution of trimethylaluminium (15.0 mL, 30.0 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **1d** (9.34 g, 15.0 mmol) in toluene (60 mL) at rt, followed by stirring at 100°C overnight. All volatiles were removed *en vacuo* and the orange solid was recrystallized from Et_2O to obtain **3d** (10.3 g, 14.1 mmol, 94%) as a white crystalline solid. ^1H NMR (400 MHz, C_6D_6): δ (ppm) = -0.74 (s, 12H, $\text{Al}(\text{CH}_3)_2$), 1.32 (d, $^3J_{\text{HH}} = 6.9 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.41 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.48 (d, $^3J_{\text{HH}} = 6.9 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 3.49 (sept, $^3J_{\text{HH}} = 6.8 \text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 4.90 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$), 7.23–7.60 (m, 10H, $\text{C}_6\text{H}_3 + \text{C}_6\text{H}_4$); $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6): δ (ppm) = -9.4 ($\text{Al}(\text{CH}_3)_2$), 23.5 ($\text{CH}(\text{CH}_3)_2$), 26.4 ($\text{CH}(\text{CH}_3)_2$), 28.2 ($\text{C}(\text{CH}_3)_3$), 28.8 ($\text{CH}(\text{CH}_3)_2$), 39.8 ($\text{C}(\text{CH}_3)_3$), 51.2 ($\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$), 123.8 ($m\text{-C}_6\text{H}_3$), 125.8 ($p\text{-C}_6\text{H}_3$), 127.7 ($m\text{-C}_6\text{H}_4$), 128.7 ($o\text{-C}_6\text{H}_4$), 129.4 ($o\text{-C}_6\text{H}_4$), 140.3 ($o\text{-C}_6\text{H}_3$), 140.8 ($i\text{-C}_6\text{H}_4$), 144.3 ($i\text{-C}_6\text{H}_3$), 179.8 ($\text{NC}(\text{C}(\text{CH}_3)_3\text{N})$); ^{27}Al NMR (104 MHz, CDCl_3): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2961 (m), 2921 (w), 2867 (w), 1413 (s), 1321 (s), 1184 (s), 669 (s); anal. calc. (found) for $[\text{C}_{46}\text{H}_{72}\text{N}_4\text{Al}_2]$: C 75.16 (75.11), H 9.87 (9.65), N 7.62 (7.61).

4a: A solution of trimethylaluminium (1.24 mL, 2.49 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **2a** (680 mg, 1.18 mmol) in toluene (10 mL) at rt, followed by stirring at 105°C overnight. Solvent concentration lead to crystallization at rt overnight to obtain **4a** (650 mg, 0.99 mmol, 80%) as a white crystalline solid. ^1H NMR (400 MHz, CDCl_3): δ (ppm) = -0.72 (s, 12H, $\text{Al}(\text{CH}_3)_2$), 1.13 (d, $^3J_{\text{HH}} = 6.8 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $^3J_{\text{HH}} = 6.9 \text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.71–1.74

(m, 8H, N(CH₂)₂(CH₂)₂), 3.09–3.14 (m, 8H, N(CH₂)₂(CH₂)₂), 3.33 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 3.44 (s, 4H, CH₂CH₂), 7.04–7.10 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = −9.5 (Al(CH₃)₂), 23.0 (CH(CH₃)₂), 25.7 (N(CH₂)₂(CH₂)₂), 25.9 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 47.5 (CH₂CH₂), 48.6 (N(CH₂)₂(CH₂)₂), 123.3 (*m*-C₆H₃), 124.5 (*p*-C₆H₃), 139.4 (*o*-C₆H₃), 144.9 (*i*-C₆H₃), 162.5 (NC(N(CH₂)₂(CH₂)₂)₃N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{−1}] = 2963 (m), 2924 (w), 2869 (vw), 1575 (w), 1461 (m), 1422 (s), 1335 (m), 1183 (s), 703 (s), 665 (vs); anal. calc. (found) for [C₄₀H₆₆N₆Al₂]: C 70.14 (69.65), H 9.71 (9.23), N 12.27 (12.91).

4b: A solution of trimethylaluminium (2.10 mL, 4.19 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **2b** (1.17 g, 1.99 mmol) in toluene (10 mL) at rt, followed by stirring at 105 °C overnight. Solvent concentration followed by layering with pentane lead to crystallization at rt overnight to obtain **4b** (1.21 g, 1.73 mmol, 87%) as clear colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = −0.72 (s, 12H, Al(CH₃)₂), 1.12 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.19 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.69–1.72 (m, 8H, N(CH₂)₂(CH₂)₂), 1.85 (qui, 2H, CH₂(CH₂)CH₂), 3.08–3.11 (m, 8H, N(CH₂)₂(CH₂)₂), 3.30–3.37 (m, 8H, CH(CH₃)₂ + CH₂(CH₂)CH₂), 7.03–7.07 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = −9.6 (Al(CH₃)₂), 23.0 (CH(CH₃)₂), 25.7 (N(CH₂)₂(CH₂)₂), 25.9 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 33.4 (CH₂(CH₂)CH₂), 43.6 (CH₂(CH₂)CH₂), 48.6 (N(CH₂)₂(CH₂)₂), 123.2 (*m*-C₆H₃), 124.5 (*p*-C₆H₃), 139.5 (*o*-C₆H₃), 144.8 (*i*-C₆H₃), 162.7 (NC(N(CH₂)₂(CH₂)₂)₃N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{−1}] = 2956 (m), 2925 (m), 2884 (w), 2864 (w), 1528 (s), 1586 (s), 1417 (s), 1327 (m), 1178 (m), 775 (s), 716 (s), 669 (s); anal. calc. (found) for [C₄₁H₆₈N₆Al₂]: C 70.45 (70.48), H 9.81 (9.54), N 12.02 (11.93).

4c: A solution of trimethylaluminium (5.25 mL, 10.1 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **2c** (3.00 g, 5.00 mmol) in toluene (10 mL) at rt, followed by stirring at 105 °C overnight. Solvent concentration lead to crystallization at rt overnight to obtain **4c** (2.97 g, 4.15 mmol, 83%) as clear colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = −0.73 (s, 12H, Al(CH₃)₂), 1.12 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.18 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.62–1.67 (m, 8H, CH₂(CH₂)₂CH₂), 1.69–1.72 (m, 8H, N(CH₂)₂(CH₂)₂), 3.08–3.11 (m, 8H, N(CH₂)₂(CH₂)₂), 3.23–3.26 (m, 4H, CH₂(CH₂)₂CH₂), 3.33 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 7.03–7.09 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = −9.5 (Al(CH₃)₂), 23.0 (CH(CH₃)₂), 25.7 (N(CH₂)₂(CH₂)₂), 25.9 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 34.3 (CH₂(CH₂)₂CH₂), 46.2 (CH₂(CH₂)₂CH₂), 48.6 (N(CH₂)₂(CH₂)₂), 123.4 (*m*-C₆H₃), 124.4 (*p*-C₆H₃), 139.5 (*o*-C₆H₃), 144.8 (*i*-C₆H₃), 162.5 (NC(N(CH₂)₂(CH₂)₂)₃N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{−1}] = 2960 (m), 2926 (m), 2885 (w), 2867 (w), 1572 (m), 1522 (m), 1444 (m), 1427 (m), 1347 (m), 1180 (m), 783 (s), 706 (s), 668 (s); anal. calc. (found) for [C₄₂H₇₀N₆Al₂]: C 70.75 (70.68), H 9.90 (9.43), N 11.79 (11.56).

4d: A solution of trimethylaluminium (3.24 mL, 6.47 mmol, 2.0 M in toluene) was added dropwise to a stirred solution of **2d** (2.00 g, 3.08 mmol) in toluene (10 mL) at rt, followed by stirring

at 105 °C overnight. All volatiles were removed under vacuum to obtain a yellow solid, which was further washed with pentane (4 × 5 mL). Recrystallization in DCM at rt overnight gave the product **4d** (2.16 g, 2.83 mmol, 92%) as clear colorless crystals. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = −0.90 (s, 12H, Al(CH₃)₂), 1.15 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.20 (d, ³J_{HH} = 6.9 Hz, 12H, CH(CH₃)₂), 1.62–1.65 (m, 8H, N(CH₂)₂(CH₂)₂), 3.04–3.07 (m, 8H, N(CH₂)₂(CH₂)₂), 3.40 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 4.44 (s, 4H, CH₂(C₆H₄)CH₂), 7.03–7.11 (m, 6H, C₆H₃), 7.29–7.38 (m, 4H, CH₂(C₆H₄)CH₂); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = −10.3 (Al(CH₃)₂), 23.0 (CH(CH₃)₂), 25.6 (N(CH₂)₂(CH₂)₂), 25.9 (CH(CH₃)₂), 27.7 (CH(CH₃)₂), 48.5 (N(CH₂)₂(CH₂)₂), 49.7 (CH₂(C₆H₄)CH₂) 123.3 (*m*-C₆H₃), 124.5 (*p*-C₆H₃), 125.5 (*o*-C₆H₄), 126.1 (*o*-C₆H₄), 128.8 (*m*-C₆H₄), 139.5 (*o*-C₆H₃), 141.9 (*i*-C₆H₄), 144.8 (*i*-C₆H₃), 162.8 (NC(N(CH₂)₂(CH₂)₂)₃N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed; IR (ATR): $\tilde{\nu}$ [cm^{−1}] = 2960 (m), 2926 (m), 2889 (w), 2865 (w), 1519 (s), 1418 (s), 1332 (s), 1177 (m), 773 (m), 709 (m), 666 (s); anal. calc. (found) for [C₄₆H₇₀N₆Al₂]: C 72.60 (72.30), H 9.27 (8.86), N 11.04 (10.72).

5a: Iodine (2.31 g, 9.10 mmol) was added to a stirred solution of **3a** (1.20 g, 1.82 mmol) in toluene (10 mL) followed by stirring for eight days at rt. All volatiles were removed *en vacuo* and the dark brown solid was extracted with DCM (2 × 10 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with pentane (5 × 10 mL). A second crop of crystals was obtained by concentration of the mother solution, crystallization and washing with pentane (7 × 10 mL). **5a** (724 mg, 0.66 mmol, 36%) was obtained as a pale brown crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.25 (s, 18H, C(CH₃)₃), 1.28 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.30 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 3.30 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 4.05 (s, 4H, CH₂CH₂), 7.11–7.23 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.6 (CH(CH₃)₂), 28.1 (CH(CH₃)₂), 28.3 (C(CH₃)₃), 40.4 (C(CH₃)₃), 47.1 (CH₂CH₂), 124.2 (*m*-C₆H₃), 127.1 (*p*-C₆H₃), 136.4 (*o*-C₆H₃), 144.8 (*i*-C₆H₃), 185.7 (NC(C(CH₃)₃)N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed. A small signal at −24.7 ppm was observed, which account for the formation of [AlI₄][−] and might be caused by slow degradation; IR (ATR): $\tilde{\nu}$ [cm^{−1}] = 2961 (m), 2927 (w), 2867 (w), 1435 (m), 1387 (s), 1182 (m), 770 (s), 694 (m), 542 (s), 433 (s); anal. calc. (found) for [C₃₆H₅₆N₄Al₂I₂]: C 39.08 (39.10), H 5.10 (5.15), N 5.06 (4.90).

5b: Iodine (6.09 g, 24.0 mmol) was added to a stirred solution of **3b** (2.69 g, 4.0 mmol) in DCM (60 mL) followed by stirring for eight days at rt. All volatiles were removed *en vacuo* and the dark brown solid was extracted with DCM (80 mL) and THF (20 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with toluene (3 × 10 mL) to afford **5b** (1.80 g, 1.6 mmol, 40%) as pale brown crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.23 (s, 18H, C(CH₃)₃), 1.25 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.28 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 2.20 (quint, ³J_{HH} = 5.9 Hz, 2H, CH₂(CH₂)CH₂), 3.28 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 3.90 (t, ³J_{HH} = 5.9 Hz, 4H, CH₂(CH₂)CH₂), 7.09–7.22 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.6 (C(CH₃)₃), 28.2

(CH(CH₃)₂), 28.3 (C(CH₃)₃), 31.5 (CH₂(CH₂)CH₂), 40.4 (C(CH₃)₃), 43.7 (CH₂(CH₂)₂CH₂), 124.1 (*m*-C₆H₃), 127.0 (*p*-C₆H₃), 136.6 (*o*-C₆H₃), 144.7 (*i*-C₆H₃), 186.1 (NC(C(CH₃)₃)N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed. A small signal at -24.8 ppm was observed, which account for the formation of [AlI₄]⁻ and might be caused by slow degradation; IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2963 (m), 2918 (w), 2869 (w), 1402 (s), 1330 (s), 1188 (s), 771 (s), 732 (m), 690 (m), 539 (s), 437 (s); anal. calc. (found) for [C₄₂H₇₂N₄Al₂·0.4 DCM]: C 38.91 (38.96), H 5.13 (5.14), N 4.85 (4.73).

5c: Iodine (4.57 g, 18.0 mmol) was added to a stirred solution of **3c** (2.75 g, 4.0 mmol) in DCM (60 mL) followed by stirring for four days at rt. All volatiles were removed *en vacuo* and the dark brown solid was extracted with DCM (80 mL) and THF (20 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with toluene (3 × 10 mL) to afford **5c** (3.16 g, 2.8 mmol, 70%) as pale brown crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.20 (s, 18H, C(CH₃)₃), 1.26 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.31 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 1.95 (quint, ³J_{HH} = 3.3 Hz, 4H, CH₂(CH₂)₂CH₂), 3.32 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 3.67 (t, ³J_{HH} = 6.0 Hz, 4H, CH₂(CH₂)₂CH₂), 7.09–7.21 (m, 6 H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.7 (C(CH₃)₃), 28.2 (CH(CH₃)₂), 28.2 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 29.4 (CH₂(CH₂)₂CH₂), 40.3 (C(CH₃)₃), 46.5 (CH₂(CH₂)₂CH₂), 124.1 (*m*-C₆H₃), 126.9 (*p*-C₆H₃), 136.8 (*o*-C₆H₃), 145.0 (*i*-C₆H₃), 185.2 (NC(C(CH₃)₃)N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed. A small signal at -24.7 ppm was observed, which account for the formation of [AlI₄]⁻ and might be caused by slow degradation; IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2961 (m), 2929 (w), 2868 (w), 1406 (s), 1344 (s), 1186 (m), 773 (s), 728 (m), 435 (s); anal. calc. (found) for [C₄₂H₇₂N₄Al₂·0.8 DCM]: C 38.76 (38.57), H 5.16 (5.35), N 4.66 (4.56).

5d: Iodine (8.12 g, 32.0 mmol) was added to a stirred solution of **3d** (5.88 g, 8.0 mmol) in toluene (80 mL) followed by stirring for four days at rt. All volatiles were removed *en vacuo* and the dark brown solid was extracted with DCM (2 × 40 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with pentane (5 × 10 mL). A second crop of crystals was obtained by concentration of the mother solution, crystallization and washing with pentane (7 × 10 mL). **5d** (6.17 g, 5.2 mmol, 65%) was obtained as a pale brown crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.26 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.29 (s, 18H, C(CH₃)₃), 1.33 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 3.36 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 4.83 (s, 4H, CH₂C₆H₄CH₂), 7.10–7.70 (m, 10H, C₆H₃ + C₆H₄); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.7 (C(CH₃)₃), 28.2 (CH(CH₃)₂), 28.3 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 40.3 (C(CH₃)₃), 50.6 (CH₂C₆H₄CH₂), 124.1 (*m*-C₆H₃), 126.9 (*p*-C₆H₃), 128.9 (*m*-C₆H₄), 126.6 (*o*-C₆H₄), 130.6 (*o*-C₆H₄), 136.7 (*o*-C₆H₃), 138.0 (*i*-C₆H₄), 144.8 (*i*-C₆H₃), 185.0 (NC(C(CH₃)₃)N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed. A small signal at -24.6 ppm was observed, which account for the formation of [AlI₄]⁻ and might be caused by slow degradation; IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2957 (m),

2939 (vw), 2874 (w), 1627 (w), 1586 (w), 1463 (m), 1404 (s), 1333 (s), 1198 (s), 771 (m), 690 (m); anal. calc. (found) for [C₄₂H₆₀N₄Al₂I₄]: C 42.66 (42.32), H 5.11 (5.38), N 4.4.76 (4.30).

6b: Iodine (1.81 g, 7.15 mmol) was added to a stirred solution of **4b** (1.00 g, 1.43 mmol) in toluene (8 mL) followed by stirring for six days at rt. All volatiles were removed *en vacuo* and the dark brown mixture of products was washed with pentane (6 × 5 mL). Recrystallization from a DCM solution layered with pentane at -25 °C gave the product **6b** as yellowish crystals in very low yields (74 mg, 0.11 mmol, 8%) after three days. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.21 (dd, ³J_{HH} = 6.8 Hz, 14H, CH(CH₃)₂), 1.75–1.80 (m, 8H, N(CH₂)₂(CH₂)₂), 2.24 (qui, 2H, CH₂(CH₂)₂CH₂), 3.00–3.29 (m, 8H, N(CH₂)₂(CH₂)₂), 3.35 (sept, ³J_{HH} = 6.9 Hz, 4H, CH(CH₃)₂), 3.58 (t, ³J_{HH} = 6.9 Hz, 4H, CH₂(CH₂)₂), 7.08–7.19 (m, 6H, C₆H₃); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.1 (CH(CH₃)₂), 25.6 (N(CH₂)₂(CH₂)₂), 27.4 (CH(CH₃)₂), 28.0 (CH(CH₃)₂), 32.3 (CH₂(CH₂)₂CH₂), 42.6 (CH₂(CH₂)₂CH₂), 49.7 (N(CH₂)₂(CH₂)₂), 123.9 (*m*-C₆H₃), 126.4 (*p*-C₆H₃), 136.0 (*o*-C₆H₃), 145.4 (*i*-C₆H₃), 163.9 (NC(N(CH₂)₂(CH₂)₂)₃N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = no signal observed. A small signal at -24.9 ppm was observed, which account for the formation of [AlI₄]⁻ and might be caused by slow degradation; IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2960 (m), 2924 (m), 2867 (w), 1546 (s), 1456 (m), 1348 (m), 1327 (m), 778 (m), 732 (m), 638 (s), 428 (m); anal. calc. (found) for [C₄₀H₆₆N₆Al₂]: even after repeated attempts no suitable elemental analysis could be obtained.

7d: A solution of ethylaluminium dichloride (5.6 mL, 10.0 mmol, 1.8 M in toluene) was added dropwise to a stirred solution of **1d** (3.11 g, 5.0 mmol) in toluene (40 mL) at rt, followed by stirring at 100 °C overnight. All volatiles were removed *en vacuo* and the pale yellow solid was recrystallized from toluene to obtain **7d** (4.02 g, 4.93 mmol, 98%) as a white crystalline solid. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 1.23 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 1.29 (s, 18H, C(CH₃)₃), 1.32 (d, ³J_{HH} = 6.7 Hz, 12H, CH(CH₃)₂), 3.26 (sept, ³J_{HH} = 6.7 Hz, 4H, CH(CH₃)₂), 4.78 (s, 4H, CH₂C₆H₄CH₂), 7.09–7.57 (m, 10H, C₆H₃ + C₆H₄); ¹³C{¹H} NMR (101 MHz, CDCl₃): δ (ppm) = 23.5 (C(CH₃)₃), 26.3 (CH(CH₃)₂), 28.4 (CH(CH₃)₂), 28.5 (CH(CH₃)₂), 40.0 (C(CH₃)₃), 50.5 (CH₂C₆H₄CH₂), 123.9 (*m*-C₆H₃), 126.7 (*p*-C₆H₃), 128.0 (*m*-C₆H₄), 128.6 (*o*-C₆H₄), 129.8 (*o*-C₆H₄), 136.9 (*o*-C₆H₃), 139.0 (*i*-C₆H₄), 144.6 (*i*-C₆H₃), 185.7 (NC(C(CH₃)₃)N); ²⁷Al NMR (104 MHz, CDCl₃): δ (ppm) = 104.06; IR (ATR): $\tilde{\nu}$ [cm⁻¹] = 2962 (m), 2927 (w), 2869 (w), 1498 (w), 1416 (vs), 1312 (vs), 1181 (s), 770 (m), 671 (vs); anal. calc. (found) for [C₄₂H₆₀N₄Al₂I₄]: even after repeated attempts no suitable elemental analysis could be obtained.

Catalytic experiments

Ring-opening polymerization of ε-caprolacton: In a glovebox, a glass vial equipped with a stir bar was charged with the catalyst (15.2 × 10⁻⁶ mol, 1 equiv., 0.007 mol L⁻¹), ε-aprolacton (0.3 mL, 30.3 × 10⁻³ mol, 200 equiv., 1.4 mol L⁻¹) and 2.1 mL of toluene. The vial was sealed with a crimp cap and taken out of the glovebox, where the mixture was stirred at 70 °C for 8 h. Then, the reaction was quenched by the addition of 2 mL of a HCl solution (5 mol L⁻¹ in ethanol) and the product was

precipitated by adding 5 mL of ethanol. The product was filtered off, washed with ethanol (2×5 mL) and dried in vacuum to a constant weight. The SEC traces are shown in Fig. S76–S91 (ESI†).

Ring-opening polymerization of L-lactide: in a glovebox, a glass vial equipped with a stir bar was charged with the catalyst 15.2×10^{-6} mol, 1 equiv., 0.01 mol L^{-1} , L-lactid (437 mg, 30.3×10^{-3} mol, 200 equiv., 2 mol L^{-1}) and 1.5 mL of toluene. The vial was sealed with a crimp cap and taken out of the glovebox, where the mixture was stirred at 80°C or 90°C for 25 h. The reaction was quenched by the addition of 2 mL of a HCl solution (5 mol L^{-1} in ethanol) and the product was precipitated by adding 5 mL of ethanol. The product was filtered off, washed with ethanol (2×5 mL) and dried in vacuum to a constant weight. The SEC traces are shown in Fig. S92–S99 (ESI†).

Conclusions

In summary, the synthesis and characterization of overall 14 dinuclear aluminium(III) bis(amidinate) and bis(guanidinate) complexes is reported and the molecular structures in solid state of eleven complexes was established by X-ray diffraction analysis. The dinuclear methyl aluminium complexes **3** and **4** are efficient catalysts for the ring-opening polymerization of ϵ -caprolactone and L-lactide, but undergo protonolysis with alcohols, which prohibits the use of acidic coinitiators. The bis(amidinate)s **3** were found to outperform their bis(guanidinate) relatives **4** with respect to activity and selectivity as higher conversions and more narrow polydispersity indices of both PCL and PLLA were observed using the former. However, no general trend with respect to the linker length has been observed.

Conflicts of interest

There are no conflicts to declare.

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