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Zinc chloride complexes with aliphatic and aromatic guanidine hybrid ligands and their activity in the ring-opening polymerisation of D,L-lactide

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Abstract: The synthesis of the new hybrid guanidine ligands TMGdmab, DMEGdmab, TMGdeab and DMEGdeab is reported. These ligands were combined with zinc chloride and the four new obtained complexes were structurally characterized by X-ray crystallography and NMR spectroscopy. Furthermore, eight new zinc chloride complexes were obtained by reaction of the hybrid guanidine ligands TMGdmae, DMEGdmae, TMGdeae, DMEGdeae, TMGdmap, DMEGdmap, TMGdeap and TEGdeap. All twelve complexes possess a tetrahedral coordination geometry. The donor situation between guanidine and amine donors was evaluated using density functional theory. These complexes show robust activity in the melt polymerization of technical unsublimed lactide. For selected complexes kinetic polymerization experiments have been performed which show first-order behavior. The end-group was proven by NMR spectroscopy.

Introduction

Polylactide (PLA) is a biodegradable plastic and the production starts from renewable raw materials such as sugar beets, starch or agricultural waste.[1-9] So it consists of 100% bio-based contents.[2] Owing to the similar mechanical properties to poly(ethylene terephthalate) (PET) and poly(propylene) (PP), PLA is a viable alternative to petrochemical based materials.[10-14] Nowadays PLA materials are used in many applications such as packaging, in biomedical fields, consumer electronics and as fibres.[11,12] Producing biodegradable polymers from renewable raw materials will reduce the use of fossil resources.

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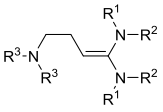
Polylactide is synthesised from lactic acid which is the starting material for the following dimerisation and ring-opening polymerisation (ROP) initiated by well-defined metal-based initiator systems.[7,15] After use, PLA can be either combusted, recycled or composted.[6,16,17] The aim is to generate PLA with controllable molecular weights and polydispersity (PD) values smaller than 1.5.[4,7] Besides, the tacticity plays an important role for the mechanical properties of the polymer.[8,18-21] A great diversity of metals and ligands has been tested as initiators/catalysts for the ROP of cyclic esters. However, the toxic tin(II) octanoate is still commercially used as initiator.[8,22] Due to the multitude of application fields a catalyst is urgently required which fulfills following properties: non-toxic, biologically tolerant, highly Lewis acidic and cost-efficient.[23,24] These requirements are met by Mg (II), Zn(II), Ca(II) and Ti(IV) complexes.[24] For the stabilisation of these metal, anionic N donor ligands such as aminophenolates,[25] β-ketiminates,[26-32] phenolate Schiff bases[33] and trispyrazolylborates[34,35] have found considerable attention as stabilising ligands for lactide ROP initiators. Furthermore, Jones *et al.* published Zr(IV), Ti(IV), Hf(IV) and Al(III) complexes based on bipyrrolidine salan proligands being active in the ROP of *rac*-lactide.[36-38] Williams *et al*. obtained excellent rates and high degrees of polymerisation with yttrium, lanthanum and lutetium phosphasalen complexes.[39-41] Moreover, they synthesised dizinc(II)-complexes bearing a Schiff base ligand and isopropyl alcohol. These complexes show initiating properties for racemic lactide with moderately high activity at room temperature in solvent.[42] The working group of Okuda investigated catalysts using the same metal centres as Jones *et al*. for the ROP of lactide.[43,44] Here, a tetradentate dianionic thio-imine diphenolate ligand featuring an ortho-phenylene core was discovered.[43] Using zinc, further metal complexes have been tested for the ROP of lactide: Di Iulio *et al*. synthesised Zn(II) silsesquioxane and Kwon *et al*. investigated the influence of Zn(II) complexes bearing camphor-based iminopyridines as pre-catalysts for the ROP of lactide.[18,45] These anionic systems exhibit sensitivity towards moisture and air which demonstrate a problem for industrial use. In addition to the ligands mentioned so far neutral and robust N donor ligands such as iminopyridines[18], trispyrazolylmethanes,[46] carbenes,[47,48] phenoxy imines,[49] amidates,[50] phosphine-modified heteroscorpionates,[51] piperidinyl-benzyl-anilines[52] and guanidines[15,53-59] are used successfully for the polymerisation. As an example,

Mehrkhodavandi *et al.* investigated the influence of neutral secondary *vs.* tertiary amine donor ligands for dinuclear indium catalysts and their activity in the ROP of lactide.[60]

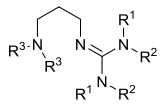
Guanidine ligands represent an import group of neutral N donor ligands, since they possess excellent donor properties, high basicity and as good coordination properties for several transition metals.[15,61-63] The guanidine ligands can differ in their bridging unit, in their guanidine moiety and in their N-donor function (Figure 1). Guanidines have been studied in various fields in chemistry: General coordination chemistry topics are investigated by the group of Himmel and Tamm.[62,64-70] For example, Tamm *et al.* investigated the impact of transition metal complexes (Ti, U, Ru, …) by basic imidazolin-2-imine N-donor ligands on the activity in polymerisation of ε-caprolactone.[68,71,72] Guanidine ligands in combination with Zn, Mg or cationic Al attract much interest as alkyl transfer reagents and (co-)catalyst in the group of Himmel.[62,64-66] Besides general coordination chemistry, guanidines are common in bioinorganic chemistry, so for tyrosinase model systems[73-80] or as model complexes for the entatic state.[81,82] Furthermore, zinc guanidine complexes are robust and highly active initiators in the ROP of lactide[53,59] and they are also active in the ATRP (atom transfer radical polymerisation) of styrene.[83-89]

Herein we report the synthesis of six hybrid guanidine ligands (DMEGdeae, DMEGdmap, TMGdmab, DMEGdmab, TMGdeab, DMEGdeab) and twelve new zinc chloride guanidine-hybrid complexes (Table 1). Eight complexes contain aliphatic ligands whereas four complexes have an aromatic backbone which allows the investigation of sterical and electronic influences. Selected complexes were tested in the polymerisation of technical, unsublimed D,L-lactide at 150 °C with no further purification of the lactide. Furthermore, DFT and NBO calculations were carried out to receive more information on the donor-acceptor properties and on the influence of the guanidine substituents.



TMG = R^1 = R^2 = -CH_3
DMEG = R^1 = -CH_3, R^2 = -CH_2CH_2-
R^3 = -CH_3, -CH_2CH_3

C_2-bridge	R_1	R_2	R_3
TMGdmae	-CH_3	-CH_3	-CH_3
DMEGdmae	-CH_3	-CH_2CH_2-	-CH_3
TMGdeae	-CH_3	-CH_3	-CH_2CH_3
DMEGdeae	-CH_3	-CH_2CH_2-	-CH_2CH_3



TMG = R^1 = R^2 = -CH_3
DMEG = R^1 = -CH_3, R^2 = -CH_2CH_2-
TEG = R^1 = R^2 = -CH_2CH_3
R^3 = -CH_3, -CH_2CH_3

C_3-bridge	R_1	R_2	R_3
TMGdmap	-CH_3	-CH_3	-CH_3
DMEGdmap	-CH_3	-CH_2CH_2-	-CH_3
TMGdeap	-CH_3	-CH_3	-CH_2CH_3
TEGdeap	-CH_2CH_3	-CH_2CH_3	-CH_2CH_3

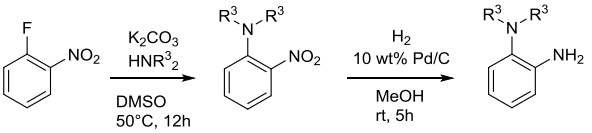
Figure 1. Overview of aliphatic hybrid guanidine ligands.

Results and Discussion

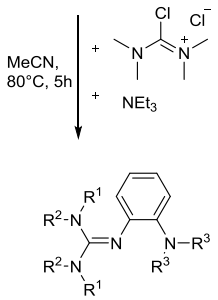
Table 1. Overview of zinc chloride complexes **C1**-**C12**.

Ligand	TMGdmae[74]	DMEGdmae[74]	TMGdeae[74]	DMEGdeae
Complex	**C1**	**C2**	**C3**	**C4**
Ligand	TMGdmap[73]	DMEGdmap	TMGdeap[73]	TEGdeap[73]
Complex	**C5**	**C6**	**C7**	**C8**
Ligand	TMGdmab	DMEGdmab	TMGdeab	DMEGdeab
Complex	**C9**	**C10**	**C11**	**C12**

The guanidine hybrid ligands TMGdmae[74], DMEGdmae[74], TMGdmap[73], DMEGdmap, TMGdeae[74], DMEGdeae, TEGdeap[73] and TMGdeap[73] were prepared by the reaction of the corresponding Vilsmeier salt *N*,*N*'-dimethylethylenchloroformamidiniumchloride, *N*,*N*,*N*',*N*'-tetramethylchloroformamidiniumchloride or *N*,*N*,*N*',*N*'-tetraethylchloroformamidiniumchloride with the appropriate primary amine. For the synthesis of TMGdmab, DMEGdmab, TMGdeab and DMEGdeab 1-fluoro-nitrobenzene was used as starting material. The first step is a nucleophilic attack of dimethylamine (dmab) or diethylamine (deab) at the carbon atom next to the flourine atom. Afterwards the nitro group is reduced in a hydrogen atmosphere with a palladium-catalyst (Scheme 1).[90] In the next step, the synthesis of the guanidine ligand follows the protocol of Herres-Pawlis *et al.* based on the protocol of Kantlehner.[76,91] To obtain the corresponding zinc complexes **C1-C12**, the ligands were combined with zinc chloride in an aprotic, dry solvent (MeCN or THF) (Table 1). Single crystals could be obtained by gas phase diffusion of diethylether or by slowly removing the solvent. Furthermore, all these complexes were identified by means of NMR and IR spectroscopy, mass spectrometry measurements as well as elemental analysis and single crystal X-ray diffraction.



Phenylene bridge	R_1	R_2	R_3
TMGdmab	-CH_3	-CH_3	-CH_3
DMEGdmab	-CH_3	-CH_2CH_2-	-CH_3
TMGdeab	-CH_3	-CH_3	-CH_2CH_3
DMEGdeab	-CH_3	-CH_2CH_2-	-CH_2CH_3



Scheme 1. Synthesis of dmab and deab ligands.[90]

Molecular structures

The molecular structures of **C1** ([Zn(TMGdmae)Cl_2]), **C2** ([Zn(DMEGdmae)Cl_2]), **C3** ([Zn(TMGdeae)Cl_2]), **C4** ([Zn(DMEGdeae)Cl_2]), **C5** ([Zn(TMGdmap)Cl_2]), **C6** ([Zn(DMEGdmap)Cl_2]), **C7** ([Zn(TMGdeap)Cl_2]), **C8** ([Zn(TEGdeap)Cl_2]), **C9** ([Zn(TMGdmab)Cl_2]), **C10** ([Zn(DMEGdmab)Cl_2]), **C11** ([Zn(TMGdeab)Cl_2]) and **C12** ([Zn(DMEGdeab)Cl_2]), were determined by single crystal X-ray diffraction. In all these zinc chloride complexes the zinc atom is fourfold coordinated by the N donor atoms of the guanidine and amine and by two chloride atoms (Fig. 2). The coordination geometry of the zinc atom possesses a distorted tetrahedral coordination environment. In all complexes the Zn-N_{gua} bond length of the guanidine unit lies between 1.99 – 2.04 Å and is thus much shorter in comparison to the Zn-N_{amine} bond lengths (2.03 –2.16 Å). The bond length of the zinc-chloride bonds is between 2.21 – 2.27 Å. The angle between the N atoms and the zinc atom depends on the backbones of the guanidine ligands. With ethylene backbone (**C1**-**C4**) the angle is between 85.6(1)° – 86.5(1)° whereas a propylene bridge (**C5**-**C8**) leads to an angle of 97.4(1)° – 98.4(1)° and an aromatic backbone (**C9**-**C12**) to an angle of 80.5(1)° – 82.5(1)° (Tab. 2). Hence, all bite angles are diminished in comparison to the ideal angle in a tetrahedral geometry of 109.5°. The angle between the coordination planes (∢ ($ZnCl_2$, ZnN_2)) of the complexes is with 83.9° – 90° (depending on the complexes) in accordance with the value expected for an ideal tetrahedral geometry of 90°. The τ_4 factor reflects the coordination geometry of the complex: In an ideal tetrahedral coordination environment the τ_4 value is 1 whereas in an square-planar coordination environment the τ_4 value is 0.[92] The zinc complexes exhibit τ_4 values in the range of 0.88 to 0.94, indicating also a tetrahedral coordination geometry. Regarding the details, the Zn-N_{gua} bond lengths of the TMG complexes (2.004(3) in **C1**, 2.012(1) in **C3**) are shorter than those of the comparable DMEG complexes (2.037(1) in **C2**, 2.034(1) in **C4**). This leads to the assumption that the TMG guanidine moiety is a stronger donor than the DMEG unit.[84,89] As reported before in all complexes, the Zn-N_{gua} bond lengths (e. g. 2.004(3) in **C1**, 2.037(1) in **C2**, 2.034(1) in **C4**, 2.013(1) in **C9)** are shorter than the comparable Zn-N_{amine} bonds (2.106(3) in **C1**, 2.089(1) in **C2**, 2.100(1) in **C4**, 2.116(1) in **C9**) (Tab. 2).[84] The reason is the stronger σ-donor character of the guanidine function.[89]

To quantify the delocalisation in the guanidine group the structural parameter ρ was introduced.[93] The parameter ρ can be obtained by using the ratio of the C_{gua}=N_{gua} bond length to the sum of the bond lengths of the C_{gua} - N_{amine} bonds. It describes how good the double bond in the guanidine moiety is delocalised. The complexes with an aromatic backbone **C9**-**C12** show by trend a larger ρ value than the aliphatic ones **C1**-**C8**. Thus the guanidine unit is slightly better delocalised in the aromatic ligands than in the aliphatic ones.[54] As next parameter, the guanidine twist is determined by the dihedral angles between the plane of three nitrogen atoms (N_{amine}- N_{gua} -N_{amine}) and (C_{amine}- C_{gua} -C_{amine}) of the guanidine unit. TMG complexes demonstrate a much higher twisting than comparable DMEG complexes.[54-56,58,74,89] This is due to the free rotation of the methyl groups next to the amine instead of the inflexibly ethylene bridge of the DMEG moiety. As an example the guanidine twist in the TMG complex **C1** is 33.7° and the comparable DMEG complex **C2** shows an angle of 14.4°.

In the complexes **C1**-**C4** and **C9**-**C12** a five-membered heterocycle is formed. The five-membered ring is in the energetically favoured envelope conformation (Fig. 3).[94] **C1** contains a plane with four atoms (Zn-N_{gua}-C-N_{amine}) with one carbon atom pointing out of this plane (0.57 Å). The conformation with **C9** displays the zinc atom 0.85 Å out of the plane (N_{gua}-N_{amine}-C-C). In **C1** we have a carbon atom in the endo position and in **C9** a zinc atom. The different arrangement is caused by the inflexible, aromatic backbone of the **C9** complex.

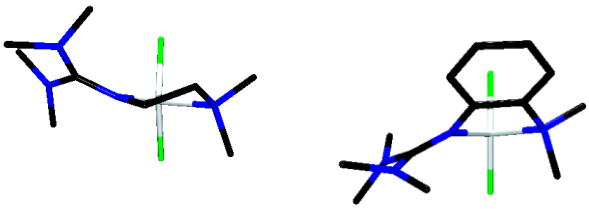


Figure 3. Different envelope conformations of the molecular structures of **C1** (left) and **C9** (right).

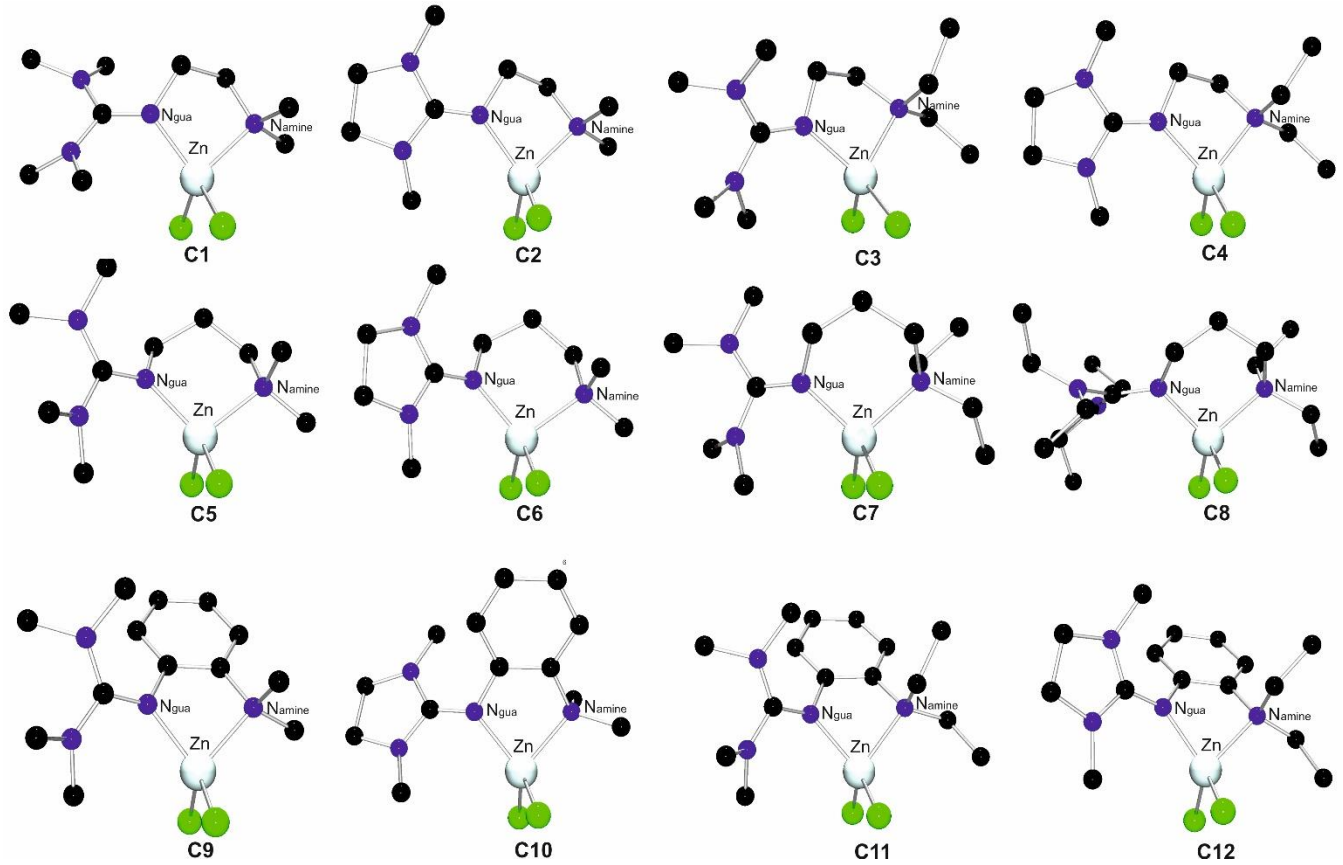


Figure 2. Molecular structures in the solid state of **C1-C12.**

Table 2. Selected bond lengths [Å] and angles [°] of **C1**-**C12**.

	C1	**C2**	**C3**	**C4**	**C5**	**C6**
Zn-N_{gua}	2.004(3)	2.037(1)	2.012(1)	2.034(1)	1.993(2)	1.997(3)
Zn-N_{amine}	2.106(3)	2.089(1)	2.033(1)	2.100(1)	2.095(2)	2.088(3)
Zn-Cl	2.234(1)	2.229(1)	2.223(1)	2.231(1)	2.227(1)	2.242(1)
	2.226(1)	2.245(1)	2.250(1)	2.242(1)	2.261(1)	2.255(1)
N-Zn-N	86.5(1)	86.3(1)	85.7(1)	85.6(1)	98.4(1)	97.5(1)
∡ ($ZnCl_2$, ZnN_2)	85.2(1)	84.3	83.9(1)	86.1(1)	87.5(1)	86.4(1)
∡ ($ZnN_{gua}N_{amine}$, CN_3)	34.1(2)	14.0	24.9(1)	11.6(1)	30.4(1)	30.7(1)
ρ[a]	0.96	0.96	0.97	0.96	0.97	0.97
τ_4[b]	0.89	0.88	0.90	0.91	0.94	0.93
Guanidine twist[c]	33.7	14.4	34.2	15.0	32.9	12.9

	C7	**C8**	**C9**	**C10**	**C11**	**C12**
Zn-N_{gua}	1.992(1)	2.002(3)	2.013(1)	2.022(1)	2.026 (2)	2.030 (2)
Zn-N_{amine}	2.111(1)	2.119(3)	2.116(1)	2.102(1)	2.158 (2)	2.139 (2)
Zn-Cl	2.251(1)	2.265(1)	2.232(1)	2.208(1)	2.214 (1)	2.215 (1)
	2.243(1)	2.231(1)	2.208(1)	2.232(1)	2.219 (1)	2.227 (1)
N-Zn-N	98.4(1)	97.4(1)	82.4 (1)	82.5(1)	80.5 (1)	81.2(1)
∡ ($ZnCl_2$, ZnN_2)	87.1(1)	87.9(1)	87.2 (1)	89.3(1)	89.7 (1)	90.0 (1)
∡ ($ZnN_{gua}N_{amine}$, CN_3)	32.2(1)	17.8(1)	27.3(1)	32.9(1)	32.7 (2)	27.2 (2)
ρ[a]	0.97	0.97	0.97	0.99	0.97	0.98
τ_4[b]	0.92	0.90	0.90	0.88	0.92	0.88
Guanidine twist[c]	34.9	37.1	32.6	9.2	32.2	7.3

[a] $\rho = \frac{2a}{(b+c)}$ with a = d(C_{gua}- N_{gua}) and b and c = d(C_{gua}- N_{amine}).[93] [b] $\tau_4 = \frac{360°-(\alpha+\beta)}{141}$.[92] [c] The dihedral angles between the planes represented by N_{gua}, $N_{amine,}$ N_{amine} and C_{gua}, $C_{Alk,}$ C_{Alk} Two twist angles for each guanidine moiety. Average value of all dihedral angles.

Density Functional Theory Calculations

In order to gain insights into the donor properties of the ligands in their complexes, quantum chemical calculations have been performed at DFT level. At first the appropriate basis set and functional have to be found. The functional TPSSh and the basis set def2-TZVP in the solvent acetonitrile with empirical dispersion correction with Becke Johnson damping turned out to be the best combination for these systems (see Table S1 in the Supporting Information). This methodology was then utilised for all complexes. In Table 3 the results of the geometry optimisations are summarised. The calculated structures are in good accordance with the molecular structures in the solid state. In the calculated structures, the Zn-N_{gua}, Zn-N_{amine} and Zn-Cl bond lengths are longer than the comparable solid-state structure bond lengths. But the trends are reflected well. As discussed before, the Zn-N_{gua} bond length in **C1** (2.025 Å) is shorter than that in **C2** (2.057 Å). In **C3** (2.042 Å) and **C4** (2.063 Å) the same trend is obtained. Additionally in the calculations, the Zn-N_{gua} bond length of the TMG unit is shorter than the comparable bond length of the DMEG unit. The calculation shows that the angles between the plane of ZnN_2 and $C_{gua}N_3$ are bigger in the aliphatic TMG complexes than in the comparable DMEG complexes. **C1** has an angle between the planes ZnN_2 and $C_{gua}N_3$ of 29.1° and **C2** of 18.7°. In case of aromatic complexes **C9**-**C12** there is no difference between TMG and DMEG systems. All the angles between the ZnN_2 and $C_{gua}N_3$ planes are nearly similar. As discussed before, the ρ-value of the complexes with aromatic systems is higher than that of aliphatic systems. **C9**-**C12** have a calculated ρ-value from 0.98-0.99 and **C1**-**C8** the value is between 0.95 and 0.97. For a more detailed analysis of the donor situation in all complexes, we performed a natural population analysis (NBO)[95-97] using the geometries obtained with the TPSSh/def2-TZVP combination. So we obtained the NBO charges and the charge transfer energies (by second order perturbation theory) for the donation from the N donor units to the zinc ion. NBO charges do not represent absolute charges but the trends give an impression of the electronic effects. The calculated charges on the zinc atoms range from 1.5 to 1.6 (Table 4). The charge on the donating N atom of the guanidine unit is in all complexes much more negative (-0.8) than that of the N atom of the amine function (-0.5). Thus, the N_{gua} atom appears more basic than the N_{amine} atom.

To elucidate the coordination properties, the donor acceptor interaction was investigated by second order perturbation theory. In **C2**, **C3**, **C6**, **C7** and **C8** the bond of the N_{gua} and N_{amine} atoms to the zinc atoms was treated as covalent bond by the NBO code and hence could not be seen as a coordinative bond and no donor-acceptor energies could be obtained. In summary, n the NBO calculations a larger donor ability of the N_{gua} lone pair of the guanidine to the zinc metal centre was obtained. This reveals stronger donor properties of the N_{gua} atom in comparison to the N_{amine} atom. Now we can compare the donor acceptor interactions of the TMG complexes with an ethylene (**C1**), propylene (**C5**) and benzene (**C9**) bridge. **C1** has a Zn-N_{gua} interaction energy of 45.5 and **C5** of 47.7 kcal/mol. The propylene bridge of **C5** leads to a slightly stronger donation of the guanidine moiety than **C1**. The interaction energy of the N_{amine} lone pair to zinc is almost the same in both cases, in **C1** 30.0 and in **C5** 30.6 kcal/mol. In comparison to **C1** and **C5**, **C9** has the lowest interaction energy for both, LP(N_{gua})-LV(Zn) (42.4 kcal/mol) and LP(N_{amine})-LV(Zn) (26.9 kcal/mol). In summary, the donor-acceptor interactions, the charge on the N atoms and the bond lengths highlight the stronger bonding ability of the N_{gua} atom in comparison to the N_{amine} atom. Furthermore, the aliphatic complexes (especially **C1** and **C5**) have by trend stronger donor properties of the nitrogen atoms to the zinc than comparable aromatic complexes (**C9**-**C12**). The reason could be the delocalised π-electron system of the aromatic system which weakens the donor properties of both nitrogen groups.

Table 3. Calculated bond lengths [Å] and angles [°] of **C1-C12** [Gaussian09, TPSSh, def2-TZVP, GD3BJ, SMD:MeCN].

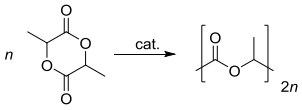
	C1	**C2**	**C3**	**C4**	**C5**	**C6**
Zn-N_{gua}	2.025	2.057	2.042	2.063	2.010	2.013
Zn-N_{amine}	2.153	2.126	2.139	2.129	2.124	2.122
Zn-Cl	2.285	2.27	2.278	2.283	2.3	2.284
	2.289	2.29	2.295	2.295	2.286	2.315
N-Zn-N	85.8	85.6	84.1	85.1	96.4	98.7
∢ ($ZnCl_2$, ZnN_2)	87.6	85.4	84.7	85.5	87.1	88.6
∢ ($ZnN_{gua}N_{amine}$, CN_3)	29.1	18.7	27.5	20.0	36.4	33.3
ρ	0.97	0.95	0.97	0.96	0.97	0.96
τ_4	0.88	0.93	0.89	0.89	0.88	0.90
	C7	**C8**	**C9**	**C10**	**C11**	**C12**
Zn-N_{gua}	2.022	2.015	2.044	2.053	2.047	2.049
Zn-N_{amine}	2.197	2.131	2.169	2.164	2.168	2.169
Zn-Cl	2.304	2.284	2.256	2.274	2.270	2.267
	2.301	2.321	2.283	2.261	2.297	2.296
N-Zn-N	97.8	98.1	80.4	79.8	80.8	80.3
∢ ($ZnCl_2$, ZnN_2)	85.6	88.3	88.2	89.1	86.6	87.9
∢ ($ZnN_{gua}N_{amine}$, CN_3)	35.8	69.9	30.5	31.1	28.5	31.1
ρ	0.97	0.97	0.98	0.98	0.99	0.99
τ_4	0.93	0.87	0.87	0.87	0.88	0.88

Table 4. Natural charge on zinc, N_{gua}, N_{amine} and Cl atoms, energies [kcal/mol] for donor-acceptor interactions for **C1-C12** [Gaussian09, TPSSh/def2-TZVP and NBO 6.0].

	C1	**C2**	**C3**	**C4**	**C5**	**C6**
Zn	1.55	1.55	1.56	1.56	1.57	1.56
N_{gua}	-0.77	-0.76	-0.78	-0.77	-0.78	-0.80
N_{amine}	-0.53	-0.53	-0.54	-0.54	-0.54	-0.54
Cl	-0.84	-0.84	-0.84	-0.84	-0.84	-0.84
	-0.85	-0.84	-0.84	-0.84	-0.85	-0.85
LP(N_{gua})-LV(Zn)	45.5	*cov*	*cov*	42.2	47.7	*cov*
LP(N_{amine})-LV(Zn)	30.0	*cov*	*cov*	29.8	30.6	*cov*
	C7	**C8**	**C9**	**C10**	**C11**	**C12**
Zn	1.57	1.57	1.56	1.56	1.55	1.56
N_{gua}	-0.79	-0.80	-0.76	-0.77	-0.77	-0.78
N_{amine}	-0.54	-0.54	-0.53	-0.53	-0.54	-0.54
Cl	-0.84	-0.83	-0.83	-0.83	-0.84	-0.84
	-0.85	-0.85	-0.84	-0.83	-0.83	-0.83
LP(N_{gua})-LV(Zn)	*cov*	*cov*	42.4	42.1	41.2	41.9
LP(N_{amine})-LV(Zn)	*cov*	*cov*	26.9	27.7	26.5	26.7

Kinetic measurements

The polymerisation of technical *rac*-lactide with the complexes **C1**, **C2**, **C5**, **C6**, **C9** and **C10** was realised in the lactide melt without any coinitiator at 150 °C and variable times. Technical, unsublimed lactide with no further purification was used with regard to the industrial applicability. These complexes were tested for the kinetic measurements, because only the influence of the bridging unit was investigated and compared. The other complexes (**C3**, **C4**, **C7**, **C8**, **C11** and **C12**) have the same bridging unit and differ only by their amine function. The monomer:catalyst ratio was chosen to be 500:1 (Scheme 2). The conversion was determined by NMR spectroscopy, and by GPC (gel permeation chromatography) the number-averaged molecular weights as well as polydispersity were analysed.



Scheme 2. ROP of lactide.

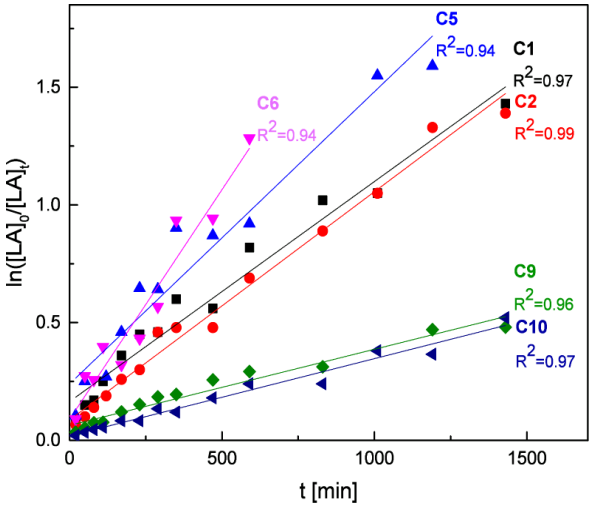


Figure 4. First-order plot of $\ln([LA]_0/[LA]_t)$ versus time [min] of **C1**, **C2**, **C5**, **C6**, **C9**, **C10** at 150°C.

Kinetic measurements were carried out to determine the order of the chain propagation and the rate constant k_{app}. The semilogarithmic relationship of the lactide concentration against the time is depicted in Figure 4. A first-order polymerisation is observed, which is in good accordance with a controlled polymerisation.[7,15,53,58,84,85,98] The zinc chloride complexes with an aromatic backbone (**C9** and **C10**) show slow activity in the polymerisation. The rate constant for **C9** and **C10** is 5.0×10^{-6} s^{-1}. The conversion after 24h is about 40% for **C9** and **C10**. Complexes with ethylene bridge polymerise faster than those with aromatic backbone. Here the rate constant k_{app} is for **C1** 1.5×10^{-5} s^{-1} and for **C2** 1.7×10^{-5} s^{-1}. With a propylene bridge in **C6** we obtained the fastest polymerisation with a k_{app} of 3.3×10^{-5} s^{-1}. Besides, a conversion of up to 80% after 14h could be reached. However, a decrease of conversion after 24h could be observed and the molecular weights decrease. The reason might be a depolymerisation after 14h. The variation of the guanidine unit (TMG or DMEG) has no significant influence on the polymerisation activity. In case of dmae and dmap the complex with DMEG is faster than with TMG unit. This trend is not obtained for dmab-complexes. In summary the dmap-complexes (**C5**, **C6**) are by trend faster in the polymerisation than dmae-complexes (**C1**, **C2**). Dmab-complexes (**C9**, **C10**) show the lowest activity for polymerisation. A large difference between these three different bridging units is the angle between zinc and the two coordinating N atoms. The angles in the complexes with a propylene bridge (**C5** and **C6)** are around 98 °, with an ethylene bridge (**C1** and **C2)** are about 86 ° and complexes with a benzene bridge (**C9** and **C10)** are 82 °. In addition, the results indicate that the bond length of the bridging group between the guanidine and amine moiety has an influence on the rate. The shorter the bridging unit the lower the polymerisation activity. **C5** and **C6** with the longest bridge (propylene) show the best conversion and **C9** and **C10** with the shortest bond (aromatic C-C-bond) lead to slow polymerisation activity. Furthermore, the donor-acceptor interaction energies, which are discussed before in the NBO analysis, are stronger for the aliphatic complexes (**C1**, **C2**, **C5**, **C6**) than of the aromatic ones (**C9**, **C10**). This could be the reason for the varying results.

Table 5. Polymerisation of lactide.[a]

	k_{app} [s^{-1}][b]	t [min]	conversion [%][c]	$M_{n,exp.}$ [g/mol][d]	$M_{n,calcd}$ [g/mol]	PD
C1	1.5×10^{-5}	830	64	19400	46000	1.52
C1	1.5×10^{-5}	1430	76	18000	54700	1.63
C2	1.7×10^{-5}	830	59	18200	42500	1.21
C2	1.7×10^{-5}	1430	75	16100	54000	1.60
C5	2.2×10^{-5}	830	70	15600	50400	1.55
C5	2.2×10^{-5}	1430	86	16600	61900	1.60
C6	3.3×10^{-5}	830	94	13000	67700	1.77
C6	3.3×10^{-5}	1430	76	13000	54700	1.58
C9	5.0×10^{-6}	830	27	-*		-
C9	5.0×10^{-6}	1430	38	-*		-
C10	5.0×10^{-6}	830	21	-*		-
C10	5.0×10^{-6}	1430	41	-*		-

* chains are too short for measuring with GPC.

[a] Polymerisation conditions: bulk, 150°C, M/I = 500/1. [b] Determined from the slope of the plots of $\ln([LA]_0/LA]_t)$ versus time. [c] Determined by integration of the methine region of the ^{1}H NMR spectrum. [d] Determined by gel permeation chromatography (GPC) in THF.

The number-averaged molecular weights are between 13000-19400 g/mol. These values differ from the theoretically calculated values which should amount to 42500-67700 g/mol. A possible reason are intramolecular and intermolecular transesterification reactions.[5] The polydispersity index is in all cases around 1.5. We relate this behaviour to water acting as coinitiator leading to more short chains.

To study the ring opening mechanism of lactide in more detail, we added to the lactide monomer and catalyst benzyl alcohol as initiator. Polymerisations were carried out in bulk at 150°C for 14 h with a ratio M/I/C (benzyl alcohol) = 500/1/1. As catalyst **C1**, **C5** and **C6** was utilised. The conversion is with the addition of benzyl alcohol by trend higher than without. The molecular weights are around half the size of the molecular weights without a coinitiator (Table 6). **C5** has a M_n with a coinitiator of 8400 g/mol and without benzyl alcohol 15600 g/mol. This leads to the assumption that the lactide monomer can be opened by the coinitiator.

To underline this statement an end group analysis via ^{1}H NMR of the polylactide was performed. The reaction time was shortened in order to obtain a smaller conversion and thus a better resolution in NMR spectroscopy. The lactide monomer was capped with a benzyloxy group (d) on one side and a hydroxyl group on the other side (b) (Figure 5). This points toward an insertion of the benzyloxy group into the lactide.[99] Besides the synthesis of polylactide, cyclic oligomers are obtained by intramolecular transesterification (x).

Table 6. Polymerisation of *rac*-lactide with the addition of the coinitiator benzyl alcohol.

[a]	conversion [%][b]	$M_{n,exp.}$ [g/mol][c]	$M_{n,calcd}$ [g/mol]	PD[c]
C1	75	8300	27000	1.55
C5	86	8400	31000	1.64
C6	81	10900	29000	1.57

[a] Polymerisation conditions: bulk, 150°C, M/I/C = 500/1/1, t = 14 h. [b] Determined by integration of the methine region of the ^{1}H NMR spectrum. [c] Determined by gel permeation chromatography (GPC) in THF.

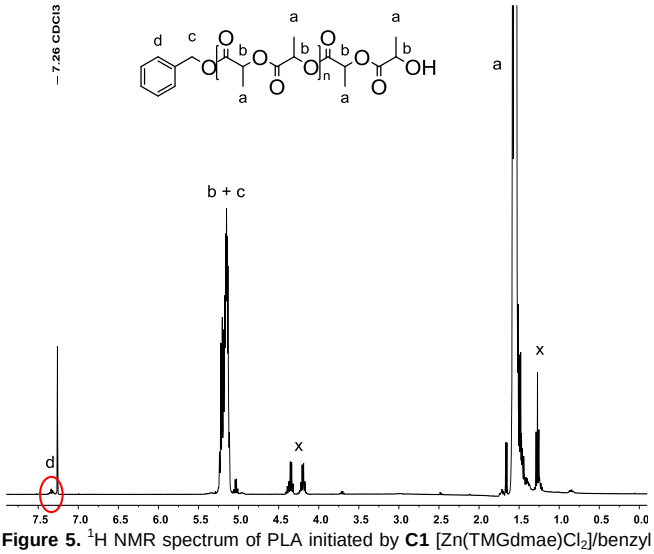


Figure 5. ^{1}H NMR spectrum of PLA initiated by **C1** [Zn(TMGdmae)Cl_2]/benzyl alcohol. Conditions: Lactide/Complex/BnOH = 500/1/1, 150 °C, 1h, conversion = 27%.

Conclusions

Herein, we presented twelve zinc chloride hybrid guanidine complexes. The ligands were generated by the reaction of two different chloroformamidinium chlorides with the corresponding primary amines. Afterwards a coordination of the ligands to the zinc chloride resulted in distorted tetrahedrally coordinated complexes. The structural trends are compared with the results of DFT calculations. The calculated and experimental structures are in good accordance when using TPSSh/def2-TZVP together with a SMD model and empirical dispersion with Becke-Johnson damping. All results indicate a stronger coordination of the guanidine N atom than the amine N atom to the zinc atom. The N_{gua}-Zn bond lengths are slightly shorter in TMG compounds than in corresponding DMEG complexes indicating that the TMG unit is the stronger donor. The guanidine twist in TMG complexes is higher because of free rotation of the methyl groups. Besides, the guanidine moiety of complexes containing an aromatic backbone are slightly better delocalised than aliphatic complexes. The aliphatic complexes show good polymerisation activity in the ring-opening polymerisation of technical unsublimed lactide proving again the superior robustness of guanidine zinc complexes. In the kinetic polymerisation measurements a first-order behaviour is observed, which is in good accordance with a coordination-insertion mechanism. It has to be noted that the complexes with an ethylene or propylene bridge are more active in the polymerisation than those with an aromatic backbone. The NBO analysis led to the results that the aliphatic backbones have higher interaction energies of the N atoms to the zinc atoms than complexes with aromatic backbones. For the end group analysis via ^{1}H NMR spectroscopy, polymerisation experiments with benzyl alcohol as coinitiator were perfomed proving the benzyl alcohol as end group. Thus, the coinitiator opened the lactide ring following a coordination-insertion mechanism.
These studies open up new design pathways to more robust zinc catalysts in lactide ROP using additional coinitiators.

Experimental Section

General: All steps were performed under nitrogen (99.996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures and also kept under nitrogen.[100] All chemicals were purchased from Sigma-Aldrich GmbH, TCI GmbH and ABCR GmbH and were used as received without further purification. D,L-lactide (Corbion Purac) was dried for three days at 40°C under *vacuo.* The precursor of the ligands TMGdmab, DMEGdmab, TMGdeab and DMEGdeab was synthesised out of 1-fluronitrobenzene.[90] *N*,*N'*-dimethylethylenechloroformamidinium chloride (DMEG-VS) and *N*,*N*,*N'*,*N'*-tetramethylchloroformamidinium chloride (TMG-VS) were synthesised as described in the literature.[76,91]

Physical Methods: Fast-atom bombardment (FAB) mass spectra were obtained with a Thermo Finnigan MAT 95 mass spectrometer for complexes **C9**-**C12**. Ionisation was achieved with accelerated xenon atoms (8kV) in glycerine or 2-nitrobenzyl alcohol matrix on a copper target. ESI spectra were recorded with a Thermo Finnigan LTQ FT Ultrafourier transform spectrometer (all ligands, **C1**, **C3**-**C5**, **C7**, **C8**). As solvent acetonitrile and water was used. Resolution was adjusted to 100000 at *m/z* 400. Depending on the method, areas between 50 und 2000 u were measured. EI spectra were obtained with a Finnigan MAT 40 mass spectrometer (**C2**).

ATR-IR spectra were measured with a Thermo Finnigan LTQ FT Ultra fourier transform spectrometer (ligands, **C1**, **C3**-**C12**) or with the FT-IR-spectrometer P510 of Nicolet as a KBr pellets (**C2**). Elemental analyses were performed with a Vario MICRO CHNS Analyser. NMR spectra were recorded on the following spectrometers: TMGdmab = Jeol EX270; DMEGdmab, TMGdeab, DMEGdeab, **C1**, **C3**-**C12 =** Jeol EX400; **C2** = Bruker Avance 500. The NMR signals were calibrated to the residual signals of the deuterated solvents ($\delta_H(CDCl_3)$ = 7.26 ppm and $\delta_H(CD_3CN)$ = 1.94 ppm).

X-ray Analyses: The crystal data for **C1** – **C12** are presented in Table 7. The data for **C1**, **C8** and **C11** were collected with an Xcalibur diffractometer from Oxford Diffraction, for **C2** with a Bruker AXS SMART APEX CCD and for **C3** – **C7**, **C9**, **C10** and **C12** with a Bruker D8 Venture APEX2 CCD using MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. Data reduction and absorption correction was performed with CRYSALIS (Oxford, 2008) and CRYSALIS RED (Oxford, 2008) for **C1**, **C8** and **C11**, with SAINT and SADABS for **C2**[101] and SAINT and SADABS for **C3** – **C7**, **C9**, **C10** and **C12**[102]. The structure was solved by direct methods and successive difference Fourier methods and all non-hydrogen atoms refined anisotropically with full-matrix least-squares based on F² (XPREP[103], SHELXTL[101] for **C2** or SHELXS-97[104] and ShelXle[105] for all other complexes). Hydrogen atoms were derived from difference Fourier maps and placed at idealised positions, riding on their parent C atoms, with isotropic displacement parameters U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(C methyl). All methyl groups were allowed to rotate but not to tip. Full crystallographic data (excluding structure factors) for

C1 to **C12** have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC – 1435628 for **C1**, CCDC – 1407092 for **C2**, CCDC – 1435629 for **C3**, CCDC – 1435630 for **C4**, CCDC – 1435631 for **C5**, CCDC – 1435632 for **C6**, CCDC – 1435633 for **C7**, CCDC –1435634 for **C8**, CCDC –1435635 for **C9**, CCDC –1435636 for **C10**, CCDC – 1435637 for **C11** and CCDC – 1435638 for **C12**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Computational details:

Density functional theory (DFT) calculations were performed with the program suite Gaussian 09.[106] The starting geometries for all complexes were generated from the molecular structures from the X-ray crystallography data. The Gaussian 09 calculations are performed with the nonlocal hybrid meta GGA TPSSh functional[107] and with the Ahlrichs type basis set def2-TZVP.[108] As solvent model, we used the SMD Model (SMD, acetonitrile)[109] as implemented in Gaussian 09. As empirical dispersion correction, we used the D3 dispersion with Becke-Johnson damping as implemented in Gaussian, Revision D.01.[110,111] For TPSSh, the values of the original paper have been substituted by the corrected values kindly provided by S. Grimme as private communication.[112] NBO calculations were accomplished using the program suite NBO 6.0.[97,95,96] Some of these calculations have been performed within the MoSGrid environment.[113-115]

Gel Permeation Chromatography (GPC):

The average molecular weights and the weight distributions of the obtained polylactide samples were determined by gel permeation chromatography (GPC) in THF as mobile phase at a flow rate of 1 mL/min. The utilised GPCmax VE-2001 from Viscotek is a combination of an HPLC pump, two Malvern Viscotek T columns (porous styrene divinylbenzene copolymer) with a maximum pore size of 500 and 5000 Å and a refractive index detector (VE-3580) and a viscometer (Viscotek 270 Dual Detector). Universal calibration was applied to evaluate the chromatographic results.

Polymerisation

At the beginning the exact mass of the catalyst (0.039 mmol) was weighed in air. Furthermore, the lactide was dried for three days at 40°C under reduced pressure (5 x 10^{-2} mbar). Afterwards in a nitrogen filled box the catalyst and the D,L-lactide (3,6-dimethyl-1,4-dioxane-2,5-dione, 2.80 g, 19.40 mmol) were weighed into a morter and the catalyst and lactide were completely homogenised. Into each of the 14 reaction vessels about 200 mg are portioned. The reaction vessels were heated at 150 °C in an oven. The starting point is when the lactide is melted. After the reaction time the vessels were allowed to cool to room temperature and dichloromethane is given to the polymer. After complete dissolving an aliquot was taken for determine the conversion via ^{1}H NMR. The PLA was precipitated in ethanol (20 mL) and dried at 50°C.

General Synthesis of guanidine-amine hybrid ligands with chloroformamidinium chlorides

To the corresponding amine (30 mmol) with trimethylamine (30 mmol) dissolved in acetonitrile (40 mL) was added dropwise the Vilsmeier salt (30 mmol) dissolved in acetonitrile (40 mL) at 0°C. Afterwards the reaction mixture was stirred to reflux overnight. After adding NaOH (30 mmol) the solvent and NEt_3 were evaporated under vacuum. For a complete deprotonation of the guanidine unit, KOH (15 mL 50 wt.-%) was added and the guanidine ligand was extracted with acetonitrile (3x30 mL). The combined organic layer was dried with Na_2SO_4 and the solvent was evaporated under reduced pressure.[76]

2-(2-(dimethylamino)benzene)-1,1,3,3-tetramethylguanidine (TMGdmab)

Green oil, yield: 4.45 g (19.2 mmol, 64%). ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C): δ = 6.76-6.90 (m, 3H, CH_{arom}), 6.49 (d, J = 7.3 Hz, 1H, CH_{arom}), 2.74 (s, 6H, CH_3), 2.66 (s, 12H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$, 25°C): δ = 158.1 (C_{gua}), 144.8 (C_{arom}), 122.1 (C_{arom}), 121.9 (C_{arom}), 120.0 (C_{arom}), 117.1 (C_{arom}), 42.9 (CH_3), 39.1 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3051 [vw (v(C-$H_{arom.}$))], 2998 [w (v(C-$H_{arom.}$))], 2930 [w (v(C-H_{aliph}))], 2850 [w (v(C-H_{aliph}))], 2817 [w (v(C-H_{aliph}))], 2769 [w (v(C-H_{aliph}))], 1600 [s (v(C=N_{gua}))], 1572 [vs (v(C=N_{gua}))], 1586 [vs (v(C=N_{gua}))], 1444 (s), 1423 (m), 1369 (vs), 1315 (m), 1290 (m), 1263 (w), 1231 (m), 1202 (m), 1134 (vs), 1100 (m), 1046 (m), 1014 (s), 944 (s), 914 (m), 848 (w), 779 (m), 750 (s), 732 (s), 693 (m) cm^{-1}. HR-MS ESI(+): *m/z* (%): calcd.: 235.1923 $[C_{13}H_{23}N_4]^+$, 190.1344 $[C_{11}H_{16}N_3]^+$, found: 235.1920 (60) $[C_{13}H_{23}N_4]^+$, 190.1340 (100) $[C_{11}H_{16}N_3]^+$.

2-(2-(dimethylamino)benzene)-1,1,3,3-dimethylethylenguanidine (DMEGdmab)

Dark purple oil, yield: 4.39 g (18.9 mmol, 63%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.75-6.85 (m, 4H, CH_{arom}), 3.25 (s, 4H, CH_2), 2.79 (s, 6H, CH_3), 2.64 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.7 (C_{gua}), 145.6 (C_{arom}), 143.1 (C_{arom}), 123.2 (C_{arom}), 121.5 (C_{arom}), 120.7 (C_{arom}), 117.1 (C_{arom}), 48.4 (CH_2), 42.8 (CH_3), 34.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3047 [w (v(C-$H_{arom.}$))], 3017 [vw (v(C-$H_{arom.}$))], 2984 [w (v(C-$H_{arom.}$))], 2936 [m (v(C-$H_{arom.}$))], 2852 [m (v(C-H_{aliph}))], 2819 [m (v(C-H_{aliph}))], 2772 [m (v(C-H_{aliph}))], 1649 [vs (v(C=N_{gua}))], 1583 (m), 1567 (m), 1483 (s), 1477 (s), 1446 (s), 1435 (s), 1410 (m), 1392 (s), 1377 (m), 1356 (m), 1314 (m), 1278 (s), 1267 (m), 1240 (m), 1227 (m), 1191 (m), 1159 (m), 1120 (m), 1097 (m), 1073 (m), 1051 (m), 1032 (s), 992 (m), 967 (m), 944 (s), 918 (m), 866 (w), 857 (m), 847 (m), 772 (m), 752 (vs), 740 (s), 707 (m), 694 (m) cm^{-1}. HR-MS ESI(+): *m/z* (%): calcd.: 233.1766 $[C_{13}H_{21}N_4]^+$, found: 233.1762 (100) $[C_{13}H_{21}N_4]^+$.

2-(2-(diethylamino)phenyl)-1,1,3,3-tetramethylguanidine (TMGdeab)

Dark purple oil, yield: 6.12 g (26.7 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.89-6.75 (m, 3H, CH_{arom}), 6.50 (dt, ^3J = 7.5 Hz, 1H, CH_{arom}), 3.18 (q, ^3J = 8.7 Hz, 7.9 Hz, 4H, CH_2), 2.65 (s, 12H, CH_3), 0.97 (t, ^3J = 7.1 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 158.6 (C_{gua}), 147.0 (C_{arom}), 142.1 (C_{arom}), 123.4 (C_{arom}), 122.9 (C_{arom}), 121.6 (C_{arom}), 120.4 (C_{arom}), 45.7 (CH_2), 40.1 (CH_3), 12.4 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3054 [vw (v(C-$H_{arom.}$))], 2968 [w (v(C-$H_{arom.}$))], 2927 [m (v(C-H_{aliph}))], 2870 [m (v(C-H_{aliph}))], 2807 [w (v(C-H_{aliph}))], 1602 [vs (v(C=N_{gua}))], 1577 [vs (v(C=N_{gua}))], 1566 [vs (v(C=N_{gua}))], 1484 (vs), 1440 (s), 1425 (m), 1403 (w), 1360 (vs), 1328 (m), 1263 (m), 1233 (s), 1201 (m), 1176 (m), 1134 (vs), 1101 (m), 1064 (m), 1049 (m), 1013 (s), 916 (w), 893 (w), 841 (w), 780 (m), 749 (s), 736 (s), 723 (m), 690 (m) cm^{-1}. HR-MS ESI(+): *m/z* (%): calcd.: 263.2236 $[C_{15}H_{28}N_4]^+$, found: 263.2228 (100) $[C_{15}H_{28}N_4]^+$, 218.1651 $[C_{13}H_{20}N_3]$, 147.0915 $[C_9H_{11}N_2]$.

***N*^{1}-(1,3-dimethylimidazolidin-2-yliden)-*N*^{2},*N*^{2}-diethylbenzene-1,2-diamin (DMEGdeab)**

Dark purple oil, yield: 6.06 g (26.1 mmol, 87%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 6.95-6.74 (m, 4H, CH_{arom}), 3.22 (s, 4H, CH_2), 3.16 (q, ^3J = 7.0 Hz, 4H, CH_2), 2.60 (s, 6H, CH_3), 0.97 (t, ^3J = 7.0 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 153.9 (C_{gua}), 145.4 (C_{arom}), 143.0 (C_{arom}), 124.3 (C_{arom}), 122.5 (C_{arom}), 121.4 (C_{arom}), 121.0 (C_{arom}), 49.1 (CH_2), 45.2 (CH_2), 35.3 (CH_3), 12.8 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3048 [vw (v(C-$H_{arom.}$))], 2967 [w (v(C-$H_{arom.}$))], 2928 [w (v(C-H_{aliph}))], 2839 [w (v(C-H_{aliph}))], 1704 (w), 1649 [vs (v(C=N_{gua}))], 1601 (m), 1582 (s), 1483 (s), 1437 (s), 1412 (m), 1390 (s), 1328 (w), 1276 (s), 1236 (s), 1196 (m), 1175 (m), 1142 (w), 1099 (m), 1072 (m), 1029 (s), 967 (m),

921 (w), 902 (vw), 878 (vw), 848 (vw), 791 (w), 748 (s), 714 (m), 691 (m) cm^{-1}. HR-MS ESI(+): *m/z* (%): calcd.: 261.2079 $[C_{15}H_{26}N_4]^+$, found: 261.2072 (100) $[C_{15}H_{26}N_4]^+$, 232.1679 $[C_{13}H_{20}N_4]$.

General Synthesis of Zinc Complexes with Guanidine Ligands:

A solution of the ligand (1 mmol), dissolved in dry acetonitrile (**C1**, **C2**, **C4**, **C6**, **C9**, **C10**, **C11**, **C12**) (2 mL) and/or tetrahydrofurane (**C1**, **C3**, **C4**, **C5**, **C6**, **C7**, **C8**) (2 mL), was added dropwise to a solution of zinc chloride (1 mmol, 0.136 g) dissolved in the same solvent as the ligand (2 mL). In the case of a clear solution, crystals could be obtained by diffusion of diethyl ether (**C1**, **C5**, **C6**, **C7**, **C11**, **C12**). If the complex precipitate, the precipitate was filtered off at high temperatures. Single crystals were obtained by slowly cooling to room temperature (**C2**, **C3**, **C4, C9, C10**) or controlled evaporisation of the solvent (**C8**).

2-(2-(dimethylamino)ethyl)-1,1,3,3-tetramethylguanidine-zinc(II)chloride [Zn(TMGdmae)Cl_2] (C1)

Colourless crystals: yield: 0.11 g (0.43 mmol, 43%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.21- 3.29 (m, 2H, CH_2), 2.95 (s, 6H, CH_3), 2.83 (s, 6H, CH_3), 2.66 - 2.74 (m, 2H, CH_2), 2.56 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 165.6 (C_{gua}), 60.5 (CH_2), 46.5 (CH_3), 44.3 (CH_2), 40.0 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3264 [vw (ν(C-H_{aliph}))], 2892 [w (ν(C-H_{aliph}))], 1623 (w), 1558 [vs (ν(C=$N_{gua.}$))], 1541 [s (ν(C=$N_{gua.}$))], 1454 (m), 1427 (m), 1399 (s), 1345 (m), 1329 (m), 1281 (w), 1239 (m), 1154 (m), 1112 (w), 1081 (m), 1060 (m), 1029 (m), 1017 (m), 985 (w), 948 (m), 917 (w), 886 (m), 856 (w), 798 (m), 769 (w), 752 (m), 714 (w), 676 (w), 619 (w), 607 (vw) cm^{-1}. MS ESI(+): m/z (%) = 187.2 (100) $[C_9H_{23}N_4]^+$ (protonated ligand). $C_9H_{22}N_4Cl_2Zn$ (322.58): calcd: C 33.5, H 6.9, N 17.4, found C 33.5, H 6.7, N 17.4.

***N*^{1}-(1,3-dimethylimidazolidin-2-ylidene)-*N*^{2},*N*^{2}-dimethylethane-1,2-diamine [Zn(DMEGdmae)Cl_2] (C2)**

Colourless crystals, yield: 0.20 g (0.74 mmol, 74%).

^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 3.57 (m, 2H, CH_2), 3.42 (s, 4H, CH_2), 3.06 (s, 6H, CH_3), 2.68 (m, 2H, CH_2), 2.51 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN, 25°C): δ = 164.0 (C_{gua}), 59.7 (CH_2), 49.6 (CH_2), 45.3 (CH_3), 44.2 (CH_2), 36.5 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2993 [w (ν(C-$H_{aliph.}$))], 2972 [w (ν(C-$H_{aliph.}$))], 2954 [m (ν(C-$H_{aliph.}$))], 2918 [m (ν(C-$H_{aliph.}$))], 2879 [m (ν(C-$H_{aliph.}$))], 2846 [w (ν(C-$H_{aliph.}$))], 2804 [w (ν(C-$H_{aliph.}$))], 1608 [vs (ν(C=$N_{gua.}$))],1508 (m), 1460 (m), 1425 (m), 1404 (m), 1385 (m), 1348 (m), 1302 (m), 1263 (m), 1184 (vw), 1159 (vw), 1105 (vw), 1084 (m), 1041 (w), 1018 (m), 980 (vw), 947 (m), 906 (w), 804 (w), 769 (w), 729 (w), 648 (vw), 611 (w), 561 (vw), 530 (vw) cm^{-1}. MS EI(+): *m/z* (%): 324 (2) $[C_9H_{20}N_4{}^{37}Cl_2{}^{66}Zn$, $C_9H_{20}N_4{}^{35}Cl^{37}Cl^{68}Zn]$, 323 (1) $[C_9H_{20}N_4{}^{35}Cl^{37}Cl^{67}Zn$, $C_8{}^{13}CH_{20}N_4{}^{35}Cl^{37}Cl^{66}Zn$, $C_8{}^{13}CH_{20}N_4{}^{35}Cl_2{}^{68}Zn]$, 322 (3) $[C_9H_{20}N_4{}^{35}Cl^{37}Cl^{66}Zn$, $C_9H_{20}N_4{}^{37}Cl_2{}^{64}Zn$, $C_9H_{20}N_4{}^{35}Cl_2{}^{68}Zn]$, 321 (1) $[C_9H_{20}N_4{}^{35}Cl_2{}^{67}Zn$, $C_8{}^{13}CH_{20}N_4{}^{35}Cl_2{}^{66}Zn$, $C_8{}^{13}CH_{20}N_4{}^{35}Cl^{37}Cl^{64}Zn]$, 320 (4) $[C_9H_{20}N_4{}^{35}Cl_2{}^{66}Zn$, $C_9H_{20}N_4{}^{35}Cl^{37}Cl^{64}Zn]$, 319 (1) $[C_8{}^{13}CH_{20}N_4{}^{35}Cl_2{}^{64}Zn]$, 318 (3) $[C_9H_{20}N_4{}^{35}Cl_2{}^{64}Zn]$, 285 (33) $[C_9H_{20}N_4ClZn]$, 283 (37) $[C_9H_{20}N_4ClZn]$, 184 (83) $[C_9H_{20}N_4]$. $C_9H_{20}N_4Cl_2Zn$ (320.57): calcd: C 33.7, H 6.3, N 17.5, found C 33.7, H 6.3, N 17.6.

2-(2-(diethylamino)ethyl)-1,1,3,3-tetramethylguanidine [Zn(TMGdeae)Cl_2] (C3)

Colourless crystals, yield: 0.21 g (0.61 mmol,61%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.24 (t, ^3J = 5.50 Hz, 2H, CH_2), 3.15 (dq, ^3J=13.9, 7.11 Hz, 2H, CH_2), 2.96 (s, 6H, CH_3), 2.83 (s, 6H, CH_3), 2.79 - 2.83 (m, 2H, CH_2), 2.70 - 2.79 (m, 2H, CH_2), 1.15 (t, ^3J = 7.1 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 165.6 (C_{gua}), 53.8 (CH_2), 44.5 (CH_2), 43.8 (CH_2), 40.1 (CH_3), 40.0 (CH_3), 8.4 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2922 [s (ν(C-H_{aliph}))], 2853 [m (ν(C-H_{aliph}))], 1736 (m), 1717 (m), 1670 (w), 1616 (m), 1558 [vs (ν(C=$N_{gua.}$))], 1531 [s (ν(C=$N_{gua.}$))], 1507 (m), 1469 (vs), 1455 (s), 1392 (vs), 1347 (m), 1309 (m), 1258 (m), 1232 (m), 1216 (m), 1157 (m), 1136 (m), 1081 (s), 1063 (s), 1036 (s), 1005 (m), 942 (w), 919 (m), 889 (m), 820 (m), 781 (s), 736 (s), 669 (m), 611 (m) cm^{-1}. MS ESI(+): *m/z* (%) = 215.4 (100) $[C_{11}H_{27}N_4]^+$ (protonated ligand). $C_{11}H_{26}N_4Cl_2Zn$ (297.27): calcd: C 37.7, H 7.5, N 16.0, found C 37.6, H 7.3, N 15.8.

***N*^{1}-(1,3-dimethylimidazolidin-2-ylidene)-*N*^{2},*N*^{2}-diethylethane-1,2-diamine [Zn(DMEGdeae)Cl_2] (C4)**

Colourless crystals, yield: 0.19 g (0.55 mmol, 55%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.52 (dd, ^3J = 6.3, 4.9 Hz, 2H, CH_2), 3.41 (s, 4H, CH_2), 3.22 - 3.12 (m, 2H, CH_2), 3.11 (s, 6H, CH_3), 2.85 - 2.70 (m, 4H, CH_2), 1.14 (t, ^3J = 7.18 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 163.6 (C_{gua}), 53.2 (CH_2), 50.0 (CH_2), 43.9 (CH_3), 43.8 (CH_2), 37.2 (CH_2), 8.2 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2942 [w (ν(C-H_{aliph}))], 1606 [vs (ν(C=$N_{gua.}$))], 1509 (m), 1489 (m), 1458 (m), 1425 (m), 1405 (m), 1384 (m), 1349 (m), 1300 (s), 1246 (m), 1156 (m), 1078 (m), 1039 (m), 1008 (m), 908 (m), 822 (m), 778 (m), 739 (s), 647 (m), 637 (m), 609 (m) cm^{-1}. MS ESI(+): *m/z* (%) = 213.4 (100) $[C_{11}H_{25}N_4]^+$ (protonated ligand). $C_{11}H_{24}Cl_2N_4Zn$ (348.62): calcd. C 37.9, H 6.9, N 16.1, found C 37.9, H 6.9, N 16.2.

2-(3-(dimethylamino)propyl)-1,1,3,3-tetramethylguanidine [Zn(TMGdmap)Cl_2] (C5)

Colourless crystals, yield: 0.30 g (0.83 mmol, 83%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.35 (t, *J* = 5.22 Hz, 2H, CH_2), 2.87 (s, 12H, CH_3), 2.52 (s, 8H, CH_3/CH_2), 1.81 (ddd, ^3J = 10.86, 6.32, 4.53 Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 166.4 (C_{gua}), 61.1 (CH_2), 50.5 (CH_2), 46.3 (CH_2), 39.8 (CH_3), 27.4 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2853 [vw (ν(C-H_{aliph}))], 1564 [vs (ν(C=$N_{gua.}$))], 1533 [s (ν(C=$N_{gua.}$))], 1462 (m), 1425 (m), 1393 (s), 1362 (w), 1343 (m), 1303 (w), 1229 (m), 1179 (w), 1154 (m), 1099 (w), 1087 (w), 1056 (m), 1030 (m), 1008 (w), 967 (m), 918 (m), 855 (m), 763 (m), 713 (w), 637 (w), 623 (w) cm^{-1}. MS ESI(+): *m/z* (%) = 301.2 (20) $[C_{10}H_{24}N_4{}^{35}Cl^{66}Zn$; $C_{10}H_{24}N_4{}^{37}Cl^{64}Zn]$, 299.2 (100) $[C_{10}H_{24}N_4{}^{35}Cl^{64}Zn]$. $C_{10}H_{24}Cl_2N_4Zn$ (336.61): calcd. C 35.7, H 7.2, N 16.6, found C 35.6, H 7.1, N 16.6.

***N*^{1}-(1,3-dimethylimidazolidin-2-ylidene)-*N*^{3},*N*^{3}-dimethylpropane-1,3-diamine [Zn(DMEGdmap)Cl_2] (C6)**

Colourless crystals, yield: 0.15 g, (0.46 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 3.56 (t, ^3J = 5.22 Hz, 2H, CH_2), 3.44 (s, 4H, CH_2), 2.98 (s, 6H, CH_3), 2.85 (d, ^3J = 5.43 Hz, 2H, CH_2), 2.52 (s, 6H, CH_3), 1.80 (q, *J* = 5.3 Hz, 2H, CH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 167.4 (C_{gua}), 61.0 (CH_2), 50.0 (CH_2), 49.2 (CH_2), 46.2 (CH_3), 37.4 (CH_3), 28.2 (CH_2) ppm. IR (ATR): $\tilde{\nu}$ = 2953 [w (ν(C-H_{aliph}))], 1737 (w), 1603 [vs (ν(C=$N_{gua.}$))], 1518 (m), 1464 (m), 1430 (m), 14060 (m), 1363 (m), 1344 (m), 1294 (m), 1229 (m), 1097 (w), 1055 (m), 1035 (m), 1010 (m), 936 (w), 912 (w), 859 (w), 775 (s), 715 (w), 683 (w), 651 (w), 619 (w), 609 (w) cm^{-1}. $C_{10}H_{22}N_4Cl_2Zn$ (334.59) calcd. C 35.9, H 6.6, N 16.7, found C 35.8, H 6.4, N 16.6.

2-(3-(diethylamino)propyl)-1,1,3,3-tetramethylguanidine [Zn(TMGdeap)Cl_2] (C7)

Colourless crystals, yield: 0.25 g (0.68 mmol, 68%).

^{1}H NMR (400 MHz, CDCl3, 25 °C): δ = 3.31 (br. s., 3H, CH_3), 3.24 (dq, ^3J = 14.07, 7.27 Hz, 2H, CH_2), 3.08 (br. s., 3H, CH_3), 2.95 - 2.90 (m, 2H, CH_2), 2.83 (s, 6H, CH_3), 2.76 (dq, *J* = 14.1, 7.1 Hz, 4H, CH_2), 1.78 (dt, ^3J

= 10.56, 5.40 Hz, 2H, CH_2), 1.13 (t, ^3J = 7.25 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 166.6 (C_{gua}), 54.4 (CH_2), 50.7 (CH_2), 44.8 (CH_2), 39.8 (CH_3), 26.4 (CH_2), 7.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2905 [w (ν(C-H_{aliph}))], 1560 [vs (ν(C=$N_{gua.}$))], 1540 [vs (ν(C=$N_{gua.}$))], 1468 (m), 1448 (m), 1427 (m), 1396 (s), 1362 (w), 1349 (m), 1324 (w), 1283 (w), 1226 (w), 1165 (m), 1150 (m), 1139 (m), 1102 (m), 1062 (w), 1045 (m), 1032 (w), 1011 (w), 962 (w), 942 (w), 907 (w), 884 (w), 822 (w), 783 (w), 765 (m), 739 (m), 718 (w), 638 (w), 622 (vw), 613 (vw), 606 (vw) cm^{-1}. MS ESI(+): *m/z* (%) = 229.0 (100) $[C_{12}H_{29}N_4]^+$ (protonated ligand). $C_{12}H_{28}N_4Cl_2Zn$ (364.66) calcd. C 39.5, H 7.74, N 15.3, found C 39.5, H 7.8, N 15.4.

2-(3-(diethylamino)propyl)-1,1,3,3-tetraethylguanidine [Zn(TEGdeap)Cl_2] (C8)

Colourless crystals, yield: 0.24 g (0.57 mmol, 57%).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* = 3.65 (br. s., 2H, CH_2), 3.24 (dt, *J* = 12.8, 6.7 Hz, 2H, CH_2), 3.20 - 3.12 (m, 2H, CH_2), 3.08 (d, ^3J = 6.05 Hz, 4H, CH_2), 2.97 - 2.86 (m, 2H, CH_2), 2.86 - 2.69 (m, 2H, CH_2), 1.75 (dt, ^3J = 10.4, 5.3 Hz, 2H, CH_2), 1.35 – 0.89 (m, 18H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ = 166.5 (C_{gua}), 54.37 (CH_2), 51.3 (CH_2), 43.6 (CH_2), 42.0 (CH_2), 26.3 (CH_2), 13.6 (d, ^3J = 18.93 Hz, CH_3), 13.1 (CH_3), 7.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2969 [m (ν(C-H_{aliph}))], 2930 [w (ν(C-H_{aliph}))], 1728 (w), 1536 [vs (ν(C=N_{gua}))], 1489 (m), 1436 (vs), 1380 (m), 1342 (m), 1284 (s), 1206 (m), 1147 (m), 1103 (m), 1073 (m), 1042 (m), 1016 (m), 1005 (m), 963 (m), 928 (m), 859 (w), 792 (m), 749 (m), 738 (m), 701 (m), 636 (w), 605 (m). MS ESI(+): *m/z* (%) = 285.3 (100) $[C_{16}H_{37}N_4]^+$ (protonated ligand). $C_{16}H_{36}N_4Cl_2Zn$ (420.77) calcd. C 45.7, H 8.6, N 13.3, found C 45.7, H 8.9, N 13.3.

2-(2-(dimethylamino)phenyl)-1,1,3,3-tetramethylguanidine-zinc(II)chloride [Zn(TMGdmab)Cl_2] (C9)

Colourless crystals, yield: 0.32 mg (0.85 mmol, 85%).

^1H NMR (400 MHz, $CDCl_3$, 25°C): *δ* = 7.35 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1H, CH_{arom}), 7.16 (ddd, *J* = 8.0, 7.4, 1.4 Hz, 1H, CH_{arom}) 7.02 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H, CH_{arom}), 6.56 (dd, ^3J = 8.0 Hz, ^4J = 1.4 Hz, 1H, CH_{arom}), 2.98 (s, 6H, CH_3), 2.89 (s, 6H, CH_3), 2.72 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): *δ* = 164.0 (C_{gua}), 142.1 (C_{arom}), 141.9 (C_{arom}), 127.7 (C_{arom}), 122.9 (C_{arom}), 121.0 (C_{arom}), 120.1 (C_{arom}), 48.9 (CH_3), 40.6 (CH_3), 40.0 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 3055 [vw (ν(C-$H_{arom.}$))], 3008 [vw (ν(C-$H_{arom.}$))], 2964 [w (ν(C-$H_{aliph.}$))], 2867 [w (ν(C-$H_{aliph.}$))], 2797 [w (ν(C-$H_{aliph.}$))], 1608 (vw), 1594 (vw), 1577 (w), 1539 [vs (ν(C=$N_{gua.}$))], 1572 [vs (ν(C=$N_{gua.}$))], 1482 (m), 1468 (m), 1453 (m), 1437 (m), 1420 (s), 1407 (m), 1393 (vs), 1343 (m), 1284 (m), 1262 (m), 1239 (m), 1205 (m), 1182 (w), 1156 (s), 1144 (m), 1115 (w), 1102 (m), 1097 (m), 1065 (w), 1041 (m), 1035 (s), 1018 (m), 983 (w), 925 (m), 862 (m), 852 (m), 815 (m), 762 (s), 749 (m), 712 (m) cm^{-1}. MS FAB(+): m/z (%) = 333.3 (84) $[C_{13}H_{22}N_4{}^{35}Cl\ {}^{64}Zn]^+$, 335.3 (76) $[C_{13}H_{22}N_4\ {}^{37}Cl{}^{64}Zn$, $C_{13}H_{22}N_4{}^{35}Cl{}^{66}Zn]\ {}^+$, 337.3 (50) $[C_{13}H_{22}N_4{}^{37}Cl{}^{66}Zn]$, 235.4 (100) $[C_{13}H_{23}N_4]^+$, 190.3 (72) $[C_{11}H_{16}N_3]^+$. MS FAB(-): *m/z* (%) = 35.5 (2) (2) [$^{35}Cl^-$], 37.5 (0.6) [$^{37}Cl^-$]. $C_{13}H_{22}N_4Cl_2Zn$ (370.63) calcd. C 42.1, H 6.0, N 15.1, found C 42.1, H 6.03, N 15.0.

2-((1,3-dimethylimidazolidin-2-ylidene)amino)-*N,N*-dimethylaniline-zinc(II)chlorid [Zn(DMEGdmab)Cl_2] (C10)

Yellow crystals, yield: 0.32 g (0.89 mmol, 89%).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* = 7.30 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, CH_{arom}), 7.13 (ddd, *J* = 8.1, 7.4, 1.5 Hz, 1H, CH_{arom}), 6.97 (ddd, *J* = 8.0, 7.4, 1.5 Hz, 1H, CH_{arom}), 6.85 (dd, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 1H, CH_{arom}), 3.65 (d, *J* = 5.7 Hz, 4H, CH_2), 2.90 (s, 6H, CH_3), 2.89 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C) *δ* = 162.6 (C_{gua}), 141.9 (C_{arom}), 141.1 (C_{arom}), 127.3 (C_{arom}), 122.3 (C_{arom}), 121.4 (C_{arom}), 120.5 (C_{arom}), 48.5 (CH_2), 48.2 (CH_3), 35.7 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2961 [w (ν(C-$H_{arom.}$))], 2901 [w (ν(C-H_{aliph}))], 2875 [w (ν(C-H_{aliph}))], 2803 [vw (ν(C-H_{aliph}))], 1599 (m), 1582 (m), 1564 [s (ν(C=$N_{gua.}$))], 1540 [vs (ν(C=$N_{gua.}$))], 1484 (s), 1458 (m), 1448 (m), 1421 (s), 1414 (m), 1410 (m), 1387 (m), 1294 (m), 1274 (m), 1235 (w), 1211 (w), 1187 (m), 1166 (m), 1160 (m), 1151 (w), 1102 (m), 1084 (w), 1044 (m), 1022 (m), 981 (m), 945 (w), 923 (s), 865 (m), 822 (m), 774 (vs), 752 (m), 742 (m), 697 (w), 611 (m) cm^{-1}. MS FAB(+): *m/z* (%) = 335.3 (39) $[C_{13}H_{20}N_4{}^{37}Cl{}^{66}Zn]$, 333.3 (59) $[C_{13}H_{20}N_4{}^{37}Cl{}^{64}Zn$, $C_{13}H_{20}N_4\ {}^{35}Cl\ {}^{66}Zn]^+$, 331.3 (65) $[C_{13}H_{20}N_4{}^{35}Cl\ {}^{64}Zn]^+$, 233.4 (100) $[C_{13}H_{21}N_4]^+$. MS FAB(-): *m/z* (%) = 37.5 (0.6) [$^{37}Cl^-$], 35.5 (2) [$^{35}Cl^-$]. $C_{13}H_{20}N_4Cl_2Zn$ (368.61) calcd. C 42.4, H 5.5, N 15.2, found C 42.5, H 5.4, N 15.1.

2-(2-(Diethylamino)phenyl)-1,1,3,3-tetramethylguanidin-zinc(II)-chloride [Zn(TMGdeab)Cl_2] (C11):

Colourless crystals; yield: 0.26 g (0.65 mmol, 65%).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* = 7.21 (d, ^3J = 8.1 Hz, 1H, CH_{arom}), 7.14 (t, ^3J = 8.3 Hz, 1H, CH_{arom}), 6.96 (t, ^3J = 8.3 Hz, 1H, CH_{arom}), 6.55(d, ^3J = 8.3 Hz, 1H, CH_{arom}), 3.22 (s, 4H, CH_2), 2.95 (s, 12H, CH_3), 1.17 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 163.8 (C_{gua}), 142.6 (C_{arom}), 138.7 (C_{arom}), 127.5 (C_{arom}), 124.1 (C_{arom}), 122.1 (C_{arom}), 120.2 (C_{arom}), 47.8 (CH_2), 40.8 (CH_3), 40.1 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2978 [vw (ν(C-$H_{arom.}$))], 2937 [vw (ν(C-$H_{aliph.}$))], 2879 [vw (ν(C-$H_{aliph.}$))], 2790 [vw (ν(C-$H_{aliph.}$))], 1631 (vw), 1541 [vs (ν(C=$N_{gua.}$))], 1475 (m), 1445 (m), 1420 (m), 1396 (s), 1343 (w), 1287 (vw), 1262 (vw), 1230 (w), 1210 (w), 1152 (m), 1118 (w), 1103 (w), 1061 (w), 1042 (w), 1029 (m), 1011 (w), 922 (vw), 886 (w), 872 (w), 849 (w), 823 (m), 811 (m), 792 (m), 776 (s), 753 (m), 729 (w), 707 (m), 668 (vw), 632 (w), 620 (w), 605 (w) cm^{-1}. MS FAB(+): *m/z* (%) = 367.1 (3) $[C_{15}H_{26}{}^{37}ClN_4{}^{68}Zn]^+$, 366.1 (3) $[C_{14}{}^{13}CH_{26}{}^{35}ClN_4{}^{68}Zn]^+$, 365.1 (10) $[C_{15}H_{26}{}^{37}ClN_4{}^{66}Zn$; $C_{15}H_{26}{}^{35}ClN_4{}^{68}Zn]^+$, 364.1 (7) $[C_{15}H_{26}{}^{35}ClN_4{}^{67}Zn$; $C_{14}{}^{13}CH_{26}{}^{35}ClN_4{}^{66}Zn$; $C_{14}{}^{13}CH_{26}{}^{37}ClN_4{}^{64}Zn]^+$, 363.1 (15) $[C_{15}H_{26}{}^{35}ClN_4{}^{66}Zn$; $C_{15}H_{26}{}^{37}ClN_4{}^{64}Zn]^+$, 362.1 (5) $[C_{14}{}^{13}CH_{26}{}^{35}ClN_4{}^{64}Zn]^+$, 361.1 (20) $[C_{15}H_{26}{}^{35}ClN_4{}^{64}Zn]^+$, 263.4 (40) $[C_{15}H_{27}N_4]^+$. HR MS FAB(+): *m/z* (%) = M = $C_{15}H_{26}Cl_2N_4Zn$: calcd. 361.1137 $[C_{15}H_{26}{}^{35}ClN_4{}^{64}Zn]^+$; found 361.1128 $[C_{15}H_{26}{}^{35}ClN_4{}^{64}Zn]^+$. $C_{15}H_{26}Cl_2N_4Zn$ (396.08): calcd. C 45.2, H 6.6, N 14.1, Cl 17.8, found C 45.0, H 6.5, N 14.0, Cl 17.7.

2-((1,3-dimethylimidazolidin-2-ylidene)amino)-*N,N*-diethylaniline-zinc(II)chloride [Zn(DMEGdeab)Cl_2] (C12)

Green crystals; yield: 0.29 g (0.73 mmol, 73%).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): *δ* = 7.26 (dd, ^3J = 8.0, 1.4 Hz, 1H, CH_{arom}), 7.14 (ddd, ^3J = 7.9, 7.4, 1.5 Hz, 1H, CH_{arom}), 6.98-6.89 (m, 2H, CH_{arom}), 3.63 -3.49 (m, 4H, CH_2), 3.28-3.07 (m, 4H, CH_2), 2.77 (s, 6H, CH_3), 1.09 (t, ^3J = 7.2 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): *δ* = 161.9 (C_{gua}), 141.3 (C_{arom}), 137.8 (C_{arom}), 126.1 (C_{arom}), 122.8 (C_{arom}), 120.5 (C_{arom}), 120.2 (C_{arom}), 47.4 (CH_2), 45.9 (CH_3), 34.2 (CH_2), 8.6 (CH_3) ppm. IR (ATR): $\tilde{\nu}$ = 2984 [vw (ν(C-$H_{arom.}$))], 2936 [vw (ν(C-$H_{aliph.}$))], 2887 [vw (ν(C-$H_{aliph.}$))], 2805 [vw (ν(C-$H_{aliph.}$))], 1598 (m), 1579 (s), 1563 [vs (ν(C=$N_{gua.}$))], 1531 (s), 1482 (s), 1463 (m), 1448 (m), 1417 (s), 1389 (m), 1378 (m), 1293 (s), 1270 (m), 1210 (m), 1154 (m), 1119 (w), 1102 (m), 1081 (w), 1037 (m), 1009 (m), 983 (w), 927 (vw), 888 (w), 858 (w), 818 (w), 797 (w), 767 (vs), 745 (s), 726 (w), 699 (w), 659 (m) cm^{-1}. MS FAB(+): *m/z* (%) = 365.1 (10) $[C_{15}H_{24}{}^{37}ClN_4{}^{68}Zn]^+$, 364.1 (10) $[C_{14}{}^{13}CH_{24}{}^{35}ClN_4{}^{68}Zn]^+$, 363.1 (30) $[C_{15}H_{24}{}^{37}ClN_4{}^{66}Zn$; $C_{15}H_{24}{}^{35}ClN_4{}^{68}Zn]^+$, 362.1 (10) $[C_{15}H_{24}{}^{35}ClN_4{}^{67}Zn$; $C_{14}{}^{13}CH_{24}{}^{35}ClN_4{}^{66}Zn$; $C_{14}{}^{13}CH_{24}{}^{37}ClN_4{}^{64}Zn]^+$, 361.1 (45) $[C_{15}H_{24}{}^{35}ClN_4{}^{66}Zn$; $C_{15}H_{24}{}^{37}ClN_4{}^{64}Zn]^+$, 360.1 (15) $[C_{14}{}^{13}CH_{24}{}^{35}ClN_4{}^{64}Zn]^+$, 359.1 (50) $[C_{15}H_{24}{}^{35}ClN_4{}^{64}Zn]^+$, 261.4 (100) $[C_{15}H_{25}N_4]^+$. MS FAB(-): *m/z* (%) = 35.0 (2) [$^{35}Cl^-$]. HR MS FAB(+): *m/z* (%) = M = $C_{15}H_{24}Cl_2N_4Zn$: calcd. 359.0980 $[C_{15}H_{24}{}^{35}ClN_4{}^{64}Zn]^+$, found: 359.0981 $[C_{15}H_{24}{}^{35}ClN_4{}^{64}Zn]^+$.

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Table 7: Crystallographic data and parameters of **C1**-**C12**

	C9	C10	C11	C12

	C1	C2	C3	C4
Empirical formula	$C_9H_{22}Cl_2N_4Zn$	$C_9H_{20}Cl_2N_4Zn$	$C_{11}H_{26}Cl_2N_4Zn$	$C_{11}H_{24}Cl_2N_4Zn$
Formula mass [gmol^{-1}]	322.58	320.56	350.63	348.61
Crystal size [mm]	0.33 × 0.26 × 0.17	0.37 × 0.32 × 0.23	0.19 × 0.11 × 0.07	0.13 × 0.10 × 0.10
T [K]	100(2)	120(0)	200(2)	100(2)
Crystal system	orthorhombic	Monoclinic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	7.719(1)	13.201(1)	7.308(1)	12.186(1)
b [Å]	13.662(1)	7.901(1)	9.869(1)	8.079(1)
c [Å]	13.723(1)	13.847(1)	23.146(1)	15.643(1)
α [°]	90	90	90	90
β [°]	90	108.89(1)	91.64(1)	93.34(1)
γ [°]	90	90	90	90
V [Å^3]	1447.2(1)	1366.5(2)	1668.6(2)	1537.5(2)
Z	4	4	4	4
$\rho_{calcd.}$ [gcm^{-3}]	1.481	1.558	1.396	1.506
μ [mm^{-1}]	2.049	2.169	1.783	1.935
λ [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	672	664	736	728
hkl range	–4≤h≤10, –16≤k≤17, –5≤l≤17	±17, ±10, ±18	±8, ±11, –26≤l≤28	±14, ±9, ±18
Reflections collected	3748	11644	27371	41567
Independent reflections	2679	3252	3100	2865
$R_{int.}$	0.0273	0.0225	0.0331	0.0374
Number of parameters	151	145	169	167
R_1 [I ≥ 2σ(*I*)]	0.0312	0.0241	0.0213	0.0190
*w*R$_2$ (all data)	0.0600	0.0620	0.0591	0.0450
Goodness-of-fit	0.993	1.064	1.365	1.077
Largest diff. peak, hole [eÅ^{-3}]	–0.426, 0.472	–0.350, 0.245	–0.293, 0.288	–0.185, 0.322

	C5	C6	C7	C8
Empirical formula	$C_{10}H_{24}Cl_2N_4Zn$	$C_{10}H_{22}Cl_2N_4Zn$	$C_{12}H_{28}Cl_2N_4Zn$	$C_{16}H_{36}Cl_2N_4Zn$
Formula mass [gmol^{-1}]	336.60	334.59	364.65	420.76
Crystal size [mm]	0.17 × 0.09 × 0.09	0.15 × 0.06 × 0.04	0.19 × 0.11 × 0.07	0.35 × 0.15 × 0.10
T [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	Orthorhombic	monoclinic	tetragonal
Space group	$P2_1/c$	$Pca2_1$	$P2_1/n$	$P\bar{4}$
a [Å]	10.592(1)	22.289(1)	10.673(1)	17.546(1)
b [Å]	9.821(1)	11.212(1)	11.246(1)	17.546(1)
c [Å]	15.174(1)	11.687(1)	14.807(1)	6.926(1)
α [°]	90	90	90	90
β [°]	104.63(1)	90	106.31(1)	90
γ [°]	90	90	90	90
V [Å^3]	1527.3(2)	2920.6(2)	1705.8(2)	2132.2(2)
Z	4	8	4	4
$\rho_{calcd.}$ [gcm^{-3}]	1.464	1.522	1.420	1.311
μ [mm^{-1}]	1.944	2.033	1.747	1.407
λ [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	704	1392	768	896
hkl range	±12, ±11, ±18	±27, ±13, ±14	±12, ±13, ±17	–21≤h≤9, –10≤k≤21, –7≤l≤8
Reflections collected	33301	23458	57714	7274
Independent reflections	2835	5900	3176	4226
$R_{int.}$	0.0377	0.0606	0.0493	0.0338
Number of parameters	160	160	178	216
R_1 [I ≥ 2σ(*I*)]	0.0229	0.0229	0.0204	0.0333
*w*R$_2$ (all data)	0.0892	0.0892	0.0509	0.0694
Goodness-of-fit	1.077	1.077	1.101	1.028
Largest diff. peak, hole [eÅ^{-3}]	–0.579, 0.639	–0.579, 0.639	–0.194, 0.331	–0.328, 0.533

Empirical formula	$C_{13}H_{22}Cl_2N_4Zn$	$C_{13}H_{20}Cl_2N_4Zn$	$C_{15}H_{26}Cl_2N_4Zn$	$C_{15}H_{24}Cl_2N_4Zn$
Formula mass [gmol^{-1}]	370.62	368.60	398.67	396.65
Crystal size [mm]	0.12 × 0.08 × 0.06	0.18 × 0.11 × 0.10	0.30 × 0.25 × 0.20	0.18 × 0.10 × 0.08
T [K]	123(2)	123(2)	173(2)	173(2)
Crystal system	monoclinic	Orthorhombic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$Pna2_1$
a [Å]	9.282(1)	9.943(1)	12.245(1)	16.201(1)
b [Å]	15.313(1)	10.311(1)	10.255(1)	10.387(1)
c [Å]	12.340(1)	15.751(1)	15.419(1)	10.524(1)
α [°]	90	90	90	90
β [°]	107.62(2)	90	109.70(1)	90
γ [°]	90	90	90	90
V [Å^3]	1671.6(2)	1614.8(2)	1822.9(2)	1771.1(2)
Z	4	4	4	4
$\rho_{calcd.}$ [gcm^{-3}]	1.473	1.516	1.453	1.488
μ [mm^{-1}]	1.785	1.847	1.642	1.690
λ [Å]	0.71073	0.71073	0.71073	0.71073
F(000)	768	760	832	824
hkl range	±12, ±20, –15≤l≤16	–13≤h≤12, ±13, ±21	±15, ±12, –19≤l≤17	–21≤h≤20, –13≤k≤12, ± 13
Reflections collected	44661	43620	10349	55977
Independent reflections	4175	4017	3707	4072
$R_{int.}$	0.0379	0.0488	0.0336	0.0477
Number of parameters	187	185	205	203
R_1 [I ≥ 2σ(*I*)]	0.0236	0.0223	0.0296	0.0217
wR_2 (all data)	0.0566	0.0466	0.0708	0.0649
Goodness-of-fit	1.058	1.032	1.051	1.210
Largest diff. peak, hole [eÅ^{-3}]	–0.222, 0.437	–0.222, 0.437	–0.323, 0.360	–0.356, 0.404

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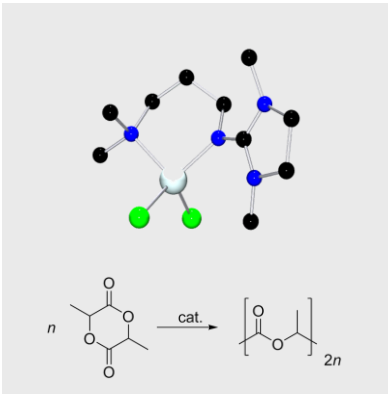
FULL PAPER

Twelve new zinc chloride complexes with hybrid guanidine ligands are reported. The structural properties of these systems were studied intensively by means of X-ray crystallography and DFT calculations. The activity in lactide polymerisation was correlated with their natural charges.



lactide polymerization*

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Zinc chloride complexes with aliphatic and aromatic guanidine hybrid ligands and their characteristic for the ring opening polymerization of D,L-lactide