Main-group metal complexes based on ditopic ligands

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Eidesstattliche Erklärung

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Andreas Rösch

This thesis was elaborated within the period from November 2017 until Oktober 2020 in the Institute of Inorganic Chemistry at the University of Regensburg, under the supervision of Prof. Dr. Robert Kretschmer and Prof. Dr. Manfred Scheer.

Parts of this work have already been published:

- A. Rösch, S. H. F. Schreiner, P. Schüller, H. Görls, R. Kretschmer 'Magnesium bis(amidinate) and bis(guanidinate) complexes: impact of the ligand backbone and bridging groups on the coordination behaviour', *Dalton Trans.* **2020**, *49*, 13072-13082.

- A. Rösch, C. M. Herzog, S. H. F. Schreiner, H. Görls and R. Kretschmer, ´Ditopic bis(*N*,*N*′,*N*′-substituted 1,2-ethanediamine) ligands: synthesis and coordination chemistry´ *Dalton Trans.* **2020**, *49*, 13818-13828.

Preface

Some of the presented results have already been published or submitted during the preparation of this thesis (vide supra). The relevant content is reprinted with the permission of the Royal Society of Chemistry. The corresponding citations and license number are given at the beginning of the respective chapters.

Each chapter includes a list of authors. At the beginning of each chapter the individual contribution of each author is described. Additionally, if some of the presented results have already been partly discussed in other theses, it is stated at the beginning of the respective chapters.

To ensure uniform design of this work, all chapters are subdivided into ‘Introduction’, ‘Results and discussion’, ‘Conclusion’, ‘References’, and ‘Supporting information’. Furthermore, all chapters have the same text settings and the numeration of compounds, figures, schemes and tables begins anew. The depicted molecular structures may differ in their style. A general ‘Introduction’ and the ‘Research Objectives’ are given at the beginning of this thesis. In addition, a comprehensive ‘Conclusion’ of this work is presented at the end of this thesis.

Dedicated to Tanja Hott

Wir ham uns oft gesehn und nie gedacht,
Wie wird es einmal sein wenn man einander nicht mehr hat,
Jetzt bist du fort und nie mehr hier,
Doch glaub mir irgendwann komme ich zu dir!

Table of contents

1. Introduction

1.1 N,N-chelating ligands in main-group element chemistry

Nowadays *N*,*N*-chelating ligands are ubiquitous in coordination chemistry. Their easy tunability regarding their steric and electronic properties as well as their bidentate nature make them potent ligands for transition metals,[1] lanthanides[2] and main-group elements.[3,4] Whereas the research field of transition metal complexes based on *N*,*N*-chelating ligands has already been well-established and widely deployed in catalysis for a long time,[5] researchers became more and more interested in main-group element chemistry during the last decades.[6] The reasons therefor are as obvious as manifold: In comparison to transition metals, main-group elements are generally less (bio)toxic, cheaper and, most important, earth-abundant.[7] Due to these properties, main-group element complexesbased on *N*,*N*-chelating ligands gain growing attention, especially in a time, where the importance of sustainability is a rising factor.

As the field of *N*,*N*-chelating ligands is a wide variety and a full review would exceed the scope of this work the following parts are focused on the three highest developed types, namely β-diketimines, amidines and guanidines, as well as the largely underdeveloped class of *N*,*N*',*N*'-substituted 1,2-ethanediamines (amidoamines), Figure 1. Here, not only the well-known mononuclear complexes, but especially the uprising research topic of dinuclear element complexes is highlighted.

Figure 1 Different types of *N,N*-chelating ligands discussed in this work.

1.1.1 β-diketimines in main-group element chemistry

Since the first description of β-diketimine based nickel(II) complexes by Parks and Holm in 1968[8] the field of application for the so called NacNac ligands is rapidly growing. Especially in main-group element coordination chemistry, NacNac ligands are responsible for several milestones in the last two decades, as depicted in the following.

Whereas the chemistry of alkaline earth metals was limited to the oxidation states of 0 and +II Jones and coworkers were able to isolate the first stable Mg(I) dimeric complexes based on guanidine- and β-diketimine ligands in 2007.[9] In comparison to traditional reducing agents like potassium mirrors or KC_8, these electronrich complexes are soluble in hydrocarbon solvents making them highly potent, easy to handle and selective reducing agents in a number of applications. Since their development they were the key for the isolation of a variety of novel compound types, which have not been accessible using traditional reducing agents before.[10]

Another remarkable example for the stabilization effects of NacNac ligands was the isolation of the cationic Lewis-base free β-diketiminate complexes of magnesium and calcium by the workgroups of Harder and Hill in 2018,[11] Figure 2. These super Lewis-acidic complexes are highly reactive towards any kind of Lewis-base and even form adducts with usually inert solvents like benzene or even silyl ether $(Me_3Si)_2O$.

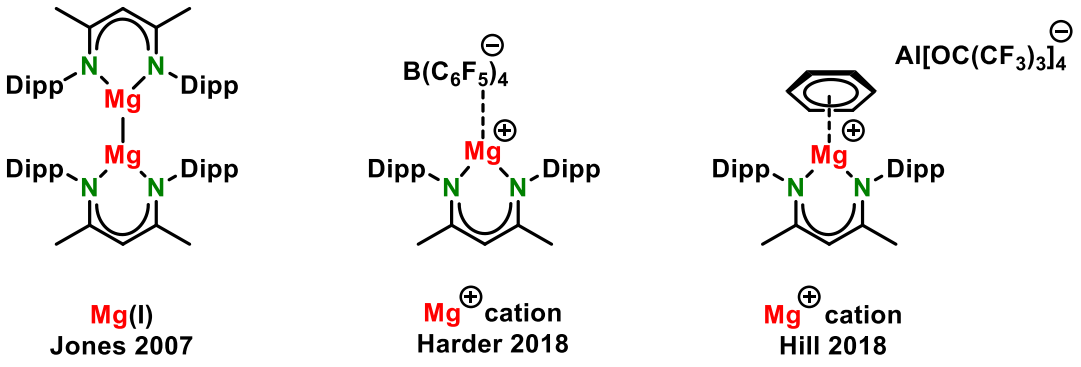
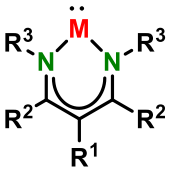


Figure 2 Selected milestone complexes in the β-diketiminate alkaline earth chemistry.

Going further to the right in the periodic table, β-diketimines also played a crucial role in the synthesis and isolation of group 13 carbene analogues. Since the first example of a stable aluminium carbene analogue by Roesky and coworkers,[12] similar complexes for gallium, indium and thallium have been reported in the following years,[13] Figure 3. Thus, β-diketimines can be considered as a door opener for a variety of powerful and important main-group element complexes.



M = Al; R^1 = H; R^2 = Me, ^{t}Bu; R^3 = Dipp
M = Ga; R^1 = H; R^2 = Me; R^3 = Dipp
M = In; R^1 = H; R^2 = Me, CF_3; R^3 = Dipp
R^1 = H; R^2 = Me; R^3 = 2,6-$Me_2C_6H_3$
R^1 = H; R^2 = Me; R^3 = 2,4,6-$Me_3C_6H_2$
M = Tl; R^1 = H; R^2 = Me; R^3 = Dipp
R^1 = H; R^2 = Me; R^3 = 2,6-$Me_2C_6H_3$
R^1 = H; R^2 = Ph; R^3 = $SiMe_3$
R^1 = Ph; R^2 = H; R^3 = Dipp

Figure 3 Carbene analogues of group 13 β-diketimine complexes.

In comparison to the above discussed β-diketimine main-group element complexes the research field of their bis(β-diketimine) analogues is a rather young and underdeveloped one. Whereas the application of the alkali metal complexes is limited as precursors for salt metathesis reactions,[14] there are a number of dinuclear alkaline-earth metal complexes, especially of Mg and Ca, known in the literature, which were applied in hydrogen elimination, copolymerization and hydroboration reactions.[15] Furthermore dinuclear complexes of Al, In and Tl have been reported recently,[4,16,17] whereupon the aluminium complexes could already proof their potential as suitable catalysts in the ring-opening polymerization of cyclic esters,[17] Figure 4.

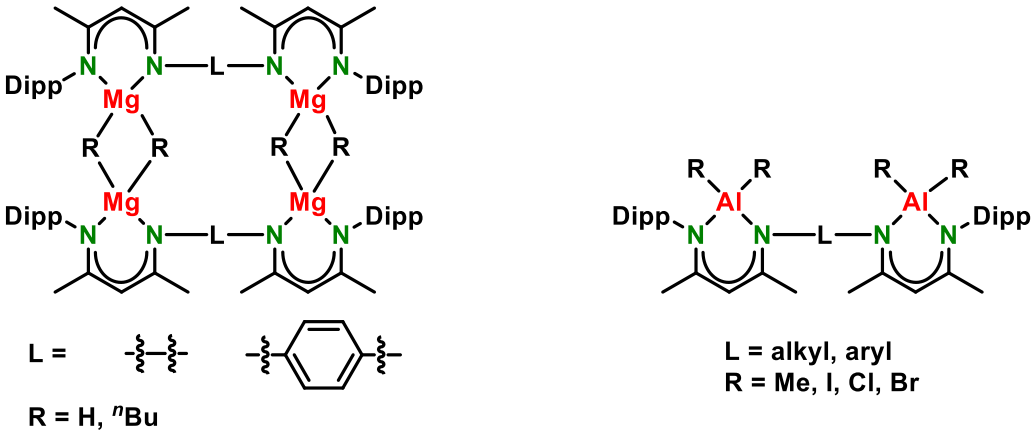
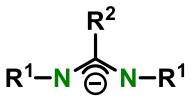


Figure 4 Examples of bis(β-diketimine) based main-group metal complexes.

1.1.2 Amidinates

The story of amidinates in metal coordination chemistry begins with the discovery of N,N,N´-tris(trimethylsilyl)benzamidine by Sanger in 1973.[18] Since then these *N*-silylated ligands evolved to ubiquitous ligands in the coordination chemistry of main-group and transition metals.[19] Starting from the mid ninetieth, an incredible variety of differently substituted amidinate ligands has been synthesized and successfully employed in coordination chemistry.[20] Their high popularity can be explained by two factors: The first one is their simple synthesis from easily prepared or commercially available starting materials. The second advantage is their high tunability in terms of electronic and steric properties. By altering the substituents at the nitrogen atoms or the carbon atom in the backbone amidinates can be easily customized to the needs of the respective application.[20]



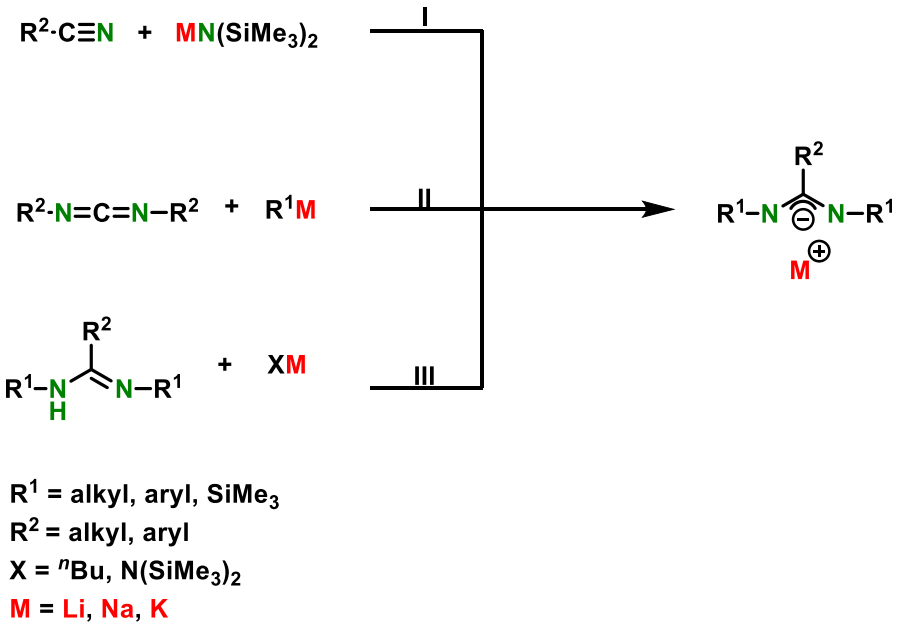
amidinate

R^1 = H, alkyl, cycloalkyl, aryl, trimethylsilyl
R^2 = H, alkyl, aryl

Figure 5 Amidinate ligand and its variety of different substituents.

1.1.2.1 Mono(amidinate)s in main-group element chemistry

Alkali metal amidinate derivatives are mainly established as starting materials in salt metathesis reactions for the isolation of further metal amidinate complexes. They are accessible via three different synthetic routes known in the literature, Scheme 1. The first pathway (**I**) is the reaction of an alkyl- or aryl carbonitrile with the respective alkali metal bis(trimethylsilyl) amide to obtain the amidinate complex involving two trimethylsilyl substituted nitrogen atoms.[21] As the diversity of thus isolated complexes is limited, two alternative routes have been developed. The addition of an organometallic compound to a carbodiimide (**II**)[22] as well as the deprotonation of an amide ligand (**III**)[23,24] represent simple reactions to access highly tunable alkali metal amidinates.



Scheme 1 Synthetic pathways to access alkali metal amidinates.

Alkaline-earth metal amidinates are generally available via the same procedures as applied for group 1 metals. However, salt metathesis reactions evolve an additional route and allow for the synthesis of heteroleptic as well as homoleptic alkaline-earth metal amidinate complexes.[25] Whereas magnesium complexes are already known in the literature for a long time,[26] researchers became interested in the isolation and stabilization of the heavier

alkaline-earth metal complexes. However, during the last decades a number of homoleptic as well as heteroleptic complexes of Ca,[25,27–29,30] Sr[27,28] and Ba[31] have been reported, which can be applied in catalysis like the intermolecular hydrophosphination of alkenes and alkynes.[29] An excellent example for the remarkable stabilization effects of bulky amidinates is the isolation of alkaline-earth metal hydrides not only for magnesium and calcium, but also for strontium.[32] Going from smaller to larger alkaline-earth metals, the metal to ligand bonds become weaker and more ionic. Consequently, these compounds have a strong propensity to participate in Schlenk-like redistribution reactions leading to a homoleptic complex (LAeL) and a metal dihydride (AeH_2). This redistribution can be circumvented by raising its kinetic barrier significantly using extremely bulky and chelating ligands, like bulky amidinates, Figure 6.

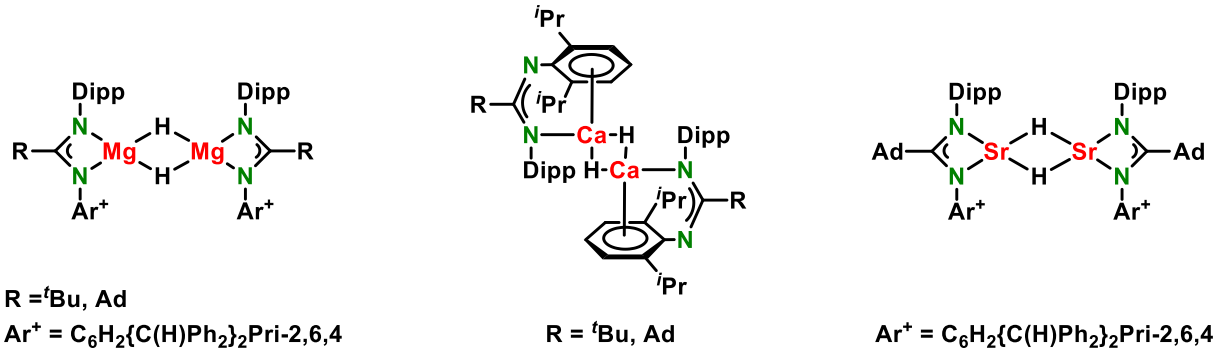


Figure 6 Examples for bulky amidinate stabilized alkaline-earth metal hydrides.

In comparison to the limited application of alkaline-earth metal amidinates in catalytic processes the use of their corresponding aluminium species is manifold. Dimethyl aluminium amidinates are commonly employed in divers polymerization reactions like ethylene polymerization,[33] ring-opening polymerizations[34,35] and copolymerizations.[35,36] Hereby, not only the neutral species, but also cationic species are at the focus of researchers, as a positive charged aluminium center is the key in many polymerization reactions. The aggregation of the aluminium cations is strongly dependent on the ligand design. Whereas smaller amidinates favor the formation of multinuclear tetra-coordinated complexes, the

bulky ligands are able to provide their mononuclear threefold coordinated cations, which show higher activity in polymerization reactions,[23] Figure 7.

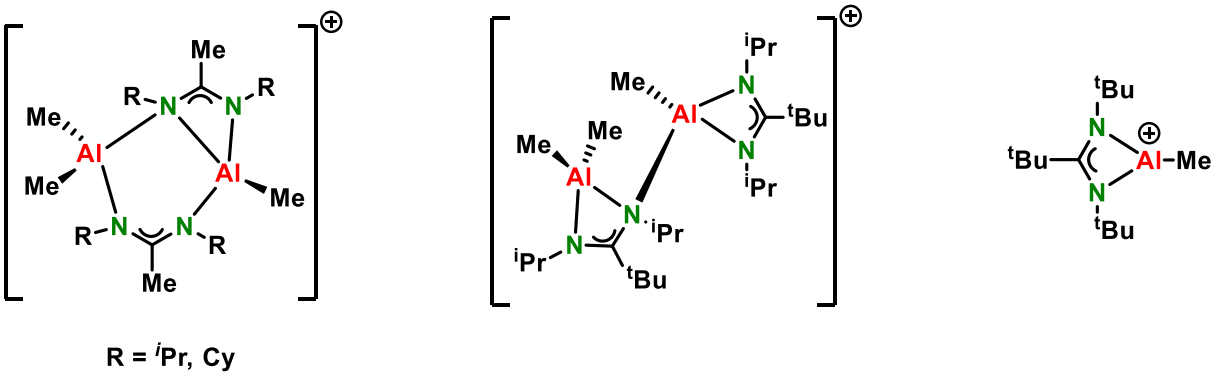


Figure 7 Different coordination modes of amidinates-based aluminium cations.

1.1.2.2 Bis(amidinates)s in main-group element chemistry

Moving on from the mononuclear amidinate complexes to the dinuclear bis(amidinate) complexes of main-group elements the amount of related publications drops dramatically. This is quite surprising as bis(amidinate) based dinuclear transition and rare-earth metal compounds have found numerous applications in material science and catalysis,[37] where they exceled their mononuclear analogs in terms of reactivity and selectivity.[38] Whereas there are several examples of alkali metal complexes as precursors for metathesis reactions,[39] only few are known for alkaline-earth metals[40] including the just recently published compounds by Jones *et al.,*[41] Figure 8.

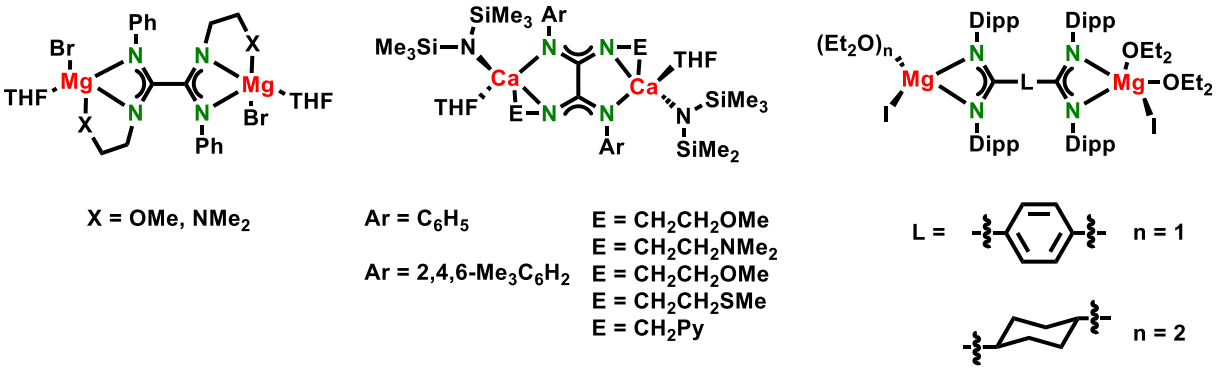


Figure 8 Bis(amidinate) alkaline-earth metal complexes published by Chen (left and middle) and Jones (right).

The same holds true for their aluminium based relatives. Even if there are some publications describing *N*,*N*- as well as backbone-bridged bis(amidinate) aluminium complexes,[42] the number compared to their mononuclear analogues is marginal. This is quite astonishing if their high potential as catalysts in polymerization reactions is taken into consideration. Whereas Lei *et al*. could not observe a cooperative effect in the polymerization of ε-caprolactone for his backbone bridged dinuclear complex,[43] it was Meléndez *et al*. who reported a significantly increased activity of the *N*,*N*-bridged dinuclear aluminium compounds compared to their mononuclear relatives in the ring-opening polymerization and copolymerization of ε-caprolactone and *L*-lactide as well as the cyclic carbonates formation from terminal epoxides and carbon dioxide.[35,44] The contrary results may be explained by the different bridging modes and thus different orientations of the two metal centers in both compounds. Whereas the backbone-bridged bis(amidinate) shows both aluminium centers pointing into opposite directions and being shielded by bulky Dipp substituents preventing an interaction to each other, the opposite is true for the *N*,*N*-bridged compounds allowing for interaction between both metal centers, Figure 9.

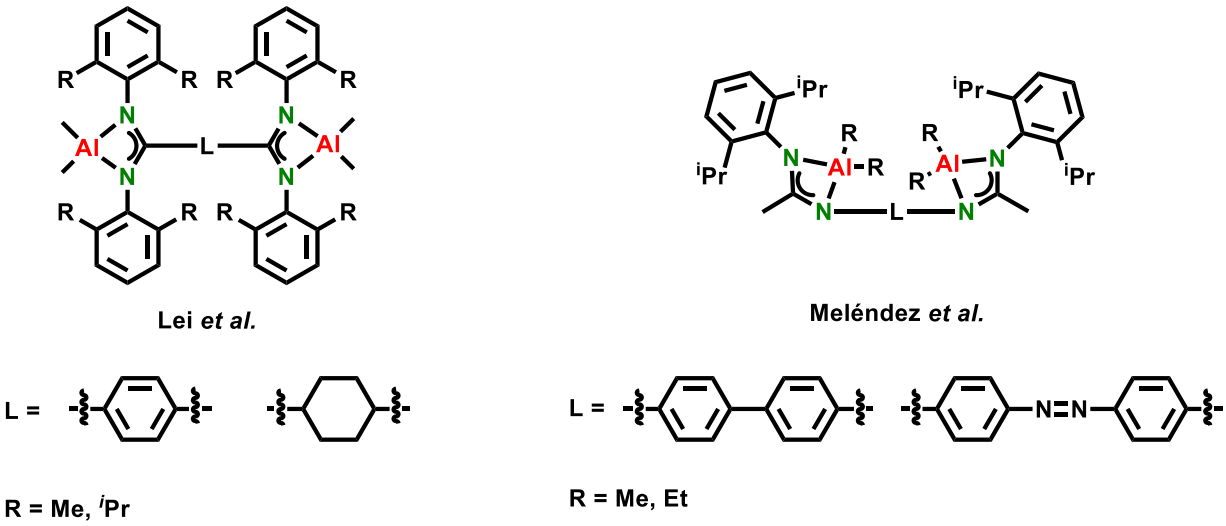


Figure 9 Dinuclear aluminium catalysts applied by Lei (left) and Meléndez (right).

1.1.3 Guanidinates

The beginning of the guanidinate coordination chemistry dates back to the year 1968, when Wade *et al.* isolated the first lithium guanidinate complex[45] followed by the first transition metal guanidinate complexes from Lappert *et al.*.[46] Since the early 1990s they are ubiquitous in coordination chemistry as they exhibit the same advantages as their closely related amidinate ligands: They are commonly easy accessible and their high tunability regarding electronic and steric properties makes them suitable ligands for elements throughout the whole periodic table.[20] Along with all the similarities guanidinates feature one decisive disparity compared to amidinates, which is their higher electron density and thus their stronger π-donor ability. By the potential of forming an iminium/diamide type resonance form, guanidinates are able to increase the electron density at the central element atom making them compatible with electron deficient element ions,[47] Figure 10.

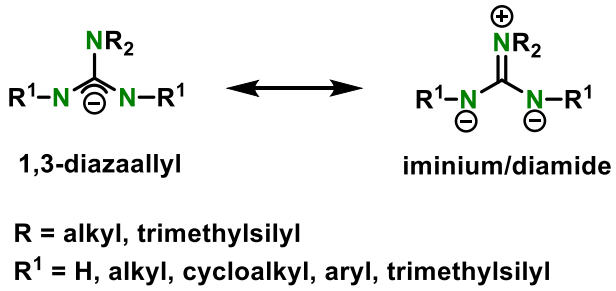


Figure 10 The 1,3-diazaallyl (left) and the iminium/diamide (right) resonance structures of guanidinates.

1.1.3.1 Mono(guanidinate)s in main-group element chemistry

Similar to the synthesis of the alkali metal amidinates, their guanidinate relatives mainly serve as precursors for metalation reactions and are accessible via two synthetic routes: The most common one is the insertion of carbodiimides into the metal-nitrogen bond of metal amide complexes.[20,47,48] As this pathway exhibits several limitations regarding sterically and electronically properties the simple deprotonation of ready prepared guanidines using alkali metal bases like ^{n}BuLi, M[N(SiMe$_3$)$_2$] or MH (M = Li, Na, K) savors rising importance.[49]

Even if the chemistry of amidinate group 2 complexes is higher developed, plenty of guanidinate-based alkaline-earth metal complexes for the non-radioactive elements, except beryllium, have been isolated during the last decades.[50,51,52–55] Notably, bulky guanidinates show the potential to withstand Schlenk-type rearrangements to a certain amount as several heteroleptic complexes of even the heavier alkaline-earth metals have been reported and successfully isolated, Figure 11. Analogous to their rich coordination chemistry their field of applications is manifold as well. Alkaline earth-metal guanidinates have been already applied as supporting ligands for transition metal complexes[56] as well as catalysts in polymerizations,[50,53] hydroaminations[55] and the Tishchenko reaction.[52,54] Anyway, the most reasonable guanidine based group 2 compound remains the already above mentioned Mg(I) dimer synthesized by Jones *et al.* in 2007,[9] Figure 11. The ability to stabilize a low-valent magnesium center in an analogous manner to β-diketiminates underlines once more the high potential that comes along with guanidinate ligands.

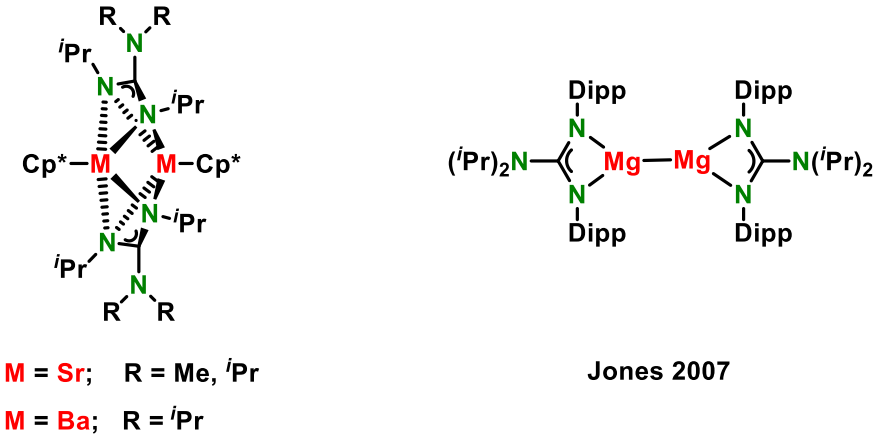


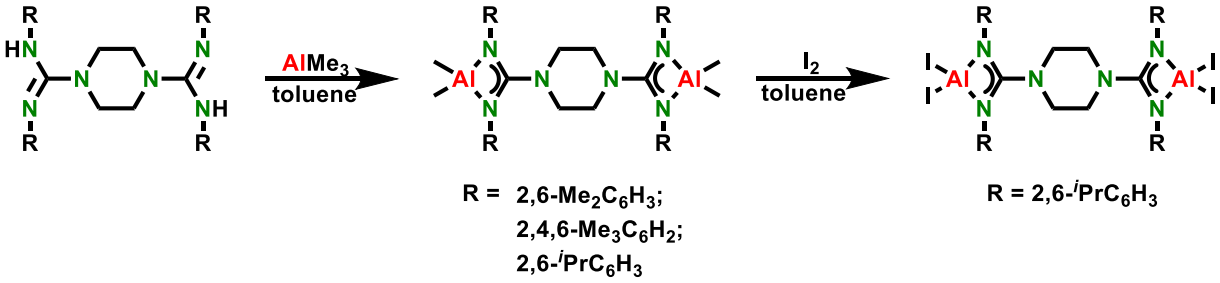
Figure 11 Examples for heteroleptic heavier alkaline earth-metal complexes (left) and Jones´ Mg(I) dimer (right).

However, the coordination chemistry and reactivity of aluminium guanidinates is, compared to their amidinate analogues, underdeveloped. There are various reports covering the isolation of alkyl, amine or halogen substituted aluminium guanidinates, but the applications remain rare.[57,58–60] Whereas aluminium guanidinate compounds have been successfully employed as catalysts in the addition of amines to carbodiimides[58,60] or the Meerwein-Ponndorf-Verley reduction,[61] experiments in hydroamination reaction remained abortive.[59]

1.1.3.2 Bis(guanidinate)s in main-group element chemistry

Talking about bis(guanidinate) main-group element complexes mainly means talking about alkali metal complexes as precursors for dinuclear lanthanide and transition metal complexes.[62] So far there are, to the best of my knowledge, no reports about the synthesis of bis(guanidinate) alkaline-earth metal complexes and only one example of dinuclear aluminium compounds published by Nembenna and coworkers in 2018.[63] Therein, they reported the isolation and characterization of a set of *N*,*N*-backbone bridged bis(guanidinate) aluminium alkyl as well as iodide complexes, Scheme 2. Even if no investigations regarding the reactivity behavior have been performed the authors are

convinced of the high potential of these species to serve as precursors for the formation of four-membered aluminium cations as well as low-valent dinuclear aluminium (I) heterocycles.



Scheme 2 Synthesis of the only yet reported dinuclear bis(guanidinate) aluminium complexes by Nembenna and coworkers.

1.1.4 Amidoamines

The term amidoamine was first defined by the group of Hagadorn and describes the ligand class of *N*,*N*´,*N*´-substituted 1,2-ethandiamines.[64] Compared to the earlier discussed *N*,*N*-chelating ligands, amidoamines exhibit several differences concerning electronic and structural properties. While for β-diketiminates, amidinates and guanidinates both nitrogen atoms can act as π and σ donors due to the delocalized electron system, in amidoamines only the deprotonated nitrogen has this ability, whereas the tertiary nitrogen can merely act as σ donor. Additionally, the opportunity to transfer stereochemical information by simply varying the substituents makes them interesting ligands for enantioselective catalysis,[65] Figure 12.

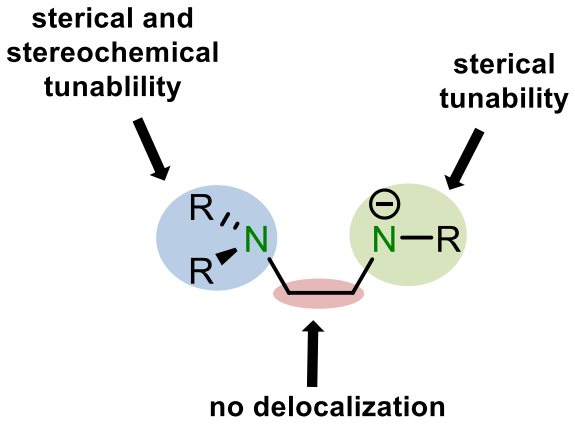


Figure 12 Special properties of amidoamine ligands.

1.1.4.1 Mono(amidoamine)s in main-group element chemistry

The first appearance of amidoamines in main-group element chemistry was reported by Zaworotko and Atwood in 1980 when they described the isolation and solution behaviour of a dimethyl aluminium complex.[66] Afterwards 33 years passed by until Deacon *et al.* employed this ligand class in the synthesis of magnesium and calcium based complexes with the goal of C–F bond activation.[67] To date there are just two more papers regarding amidoamines: The first one is an extensive report about the synthesis of versatile substituted amidoamines and the formation of their respective lithium, aluminium and gallium coordination compounds by Kretschmer *et al.*.[65] The second one was published by Crimmin and coworkers who synthesized several amidoamine-based boron hydride complexes and applied them in hydroboration and hydrodeflurionation reactions,[68] Figure 13.

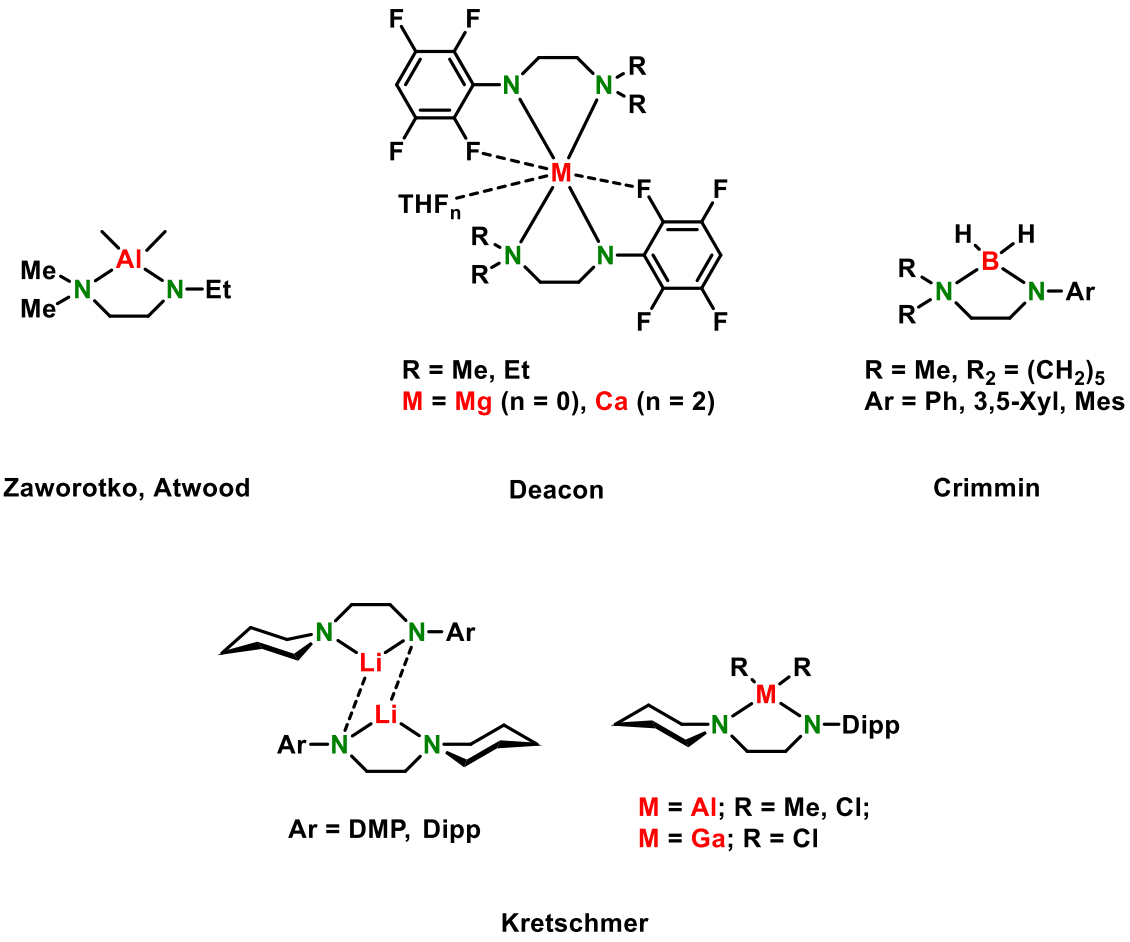


Figure 13 All yet reported amidoamine main-group element complexes, with NR_2 R ≠ **H.**

1.1.4.2 Bis(amidoamine)s in main-group element chemistry

The trend of less investigated dinucleating ligands compared to their mononucleating analogues also continues for amidoamines. While still a few mono(amidoamine) main-group element complexes are reported there is to date only one report by Hagadorn about bis(amidoamine) main-group metal compounds.[64] Therein, he describes the synthesis of lithium, aluminium and zinc derivatives based on dibenzofuran-bridged bis(amidoamine) ligands, Figure 14. Until now, no further investigations concerning the aluminium complex have been performed. This is rather surprising as its zinc relatives were intensively explored and a number of useful applications have been published throughout the last years.[69] These

results show, that bis(amidoamine)s are a yet heavily underdeveloped but promising class of ligands and their main-group element complexes could offer a high potential for a multitude of catalytic transformations.

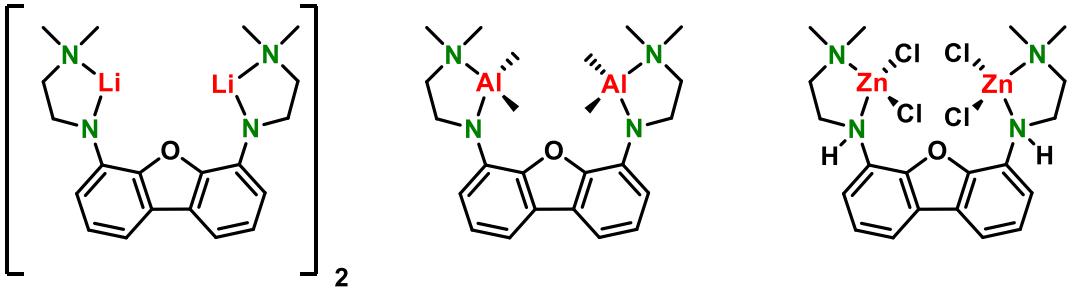


Figure 14 Bis(amidoamine) based metal complexes reported by Hagadorn and coworkers.

1.2 The cooperative effect in catalysis

The cooperative effect, also known as the 1+1>2-effect, describes the synergism between two elements in chemical and biological transformations.[70] As a result, the dinuclear systems are able to clearly exceed their normal scope of reactivity and prominent examples, like $LiAlH_4$ or the Lochmann-Schlosser superbase are widely used. However, these simple mixtures represent only a minuscule part of what is called “alkali-metal-mediated” chemistry. This research area occupies the synergistic effects within complexes bearing alkaline metals combined with further metals from the groups 1, 2, 12 or 13. The alkali-metal mediated complexes prove impressively the power of synergistic effects as their field of applications is already manifold and still continuously growing.[71]

Besides the investigations of multimetallic complexes based on monodentate ligands, also the development of novel, well-defined dinuclear complexes is a highly desirable topic. The requirement to induce cooperative effects throughout this complexes is a suitable metal-metal separation, which appears to be in an optimum range between 3.5 and 6 Å according to Feringa *et al.*.[72] The substrate activation induced by dinuclear complexes can take place in two different ways: The first one is the coordination of the unactivated substrates A and B

to the active sides of the dinuclear catalyst (synergistic activation). Consequently, the HOMO (highest occupied molecular orbital) of A increases (A*) while the LUMO (lowest unoccupied molecular orbital) of B decreases (B*) causing the formation of two reactive substrates in close proximity to each other. The second one is the simultaneously double activation of substrate A by both active sides leading to a highly activated A*, which can further react with the unactivated substrate B, Figure 15. These effects enable chemical reactions that are impossible or inefficient using traditional mono-catalysis methods.[73]

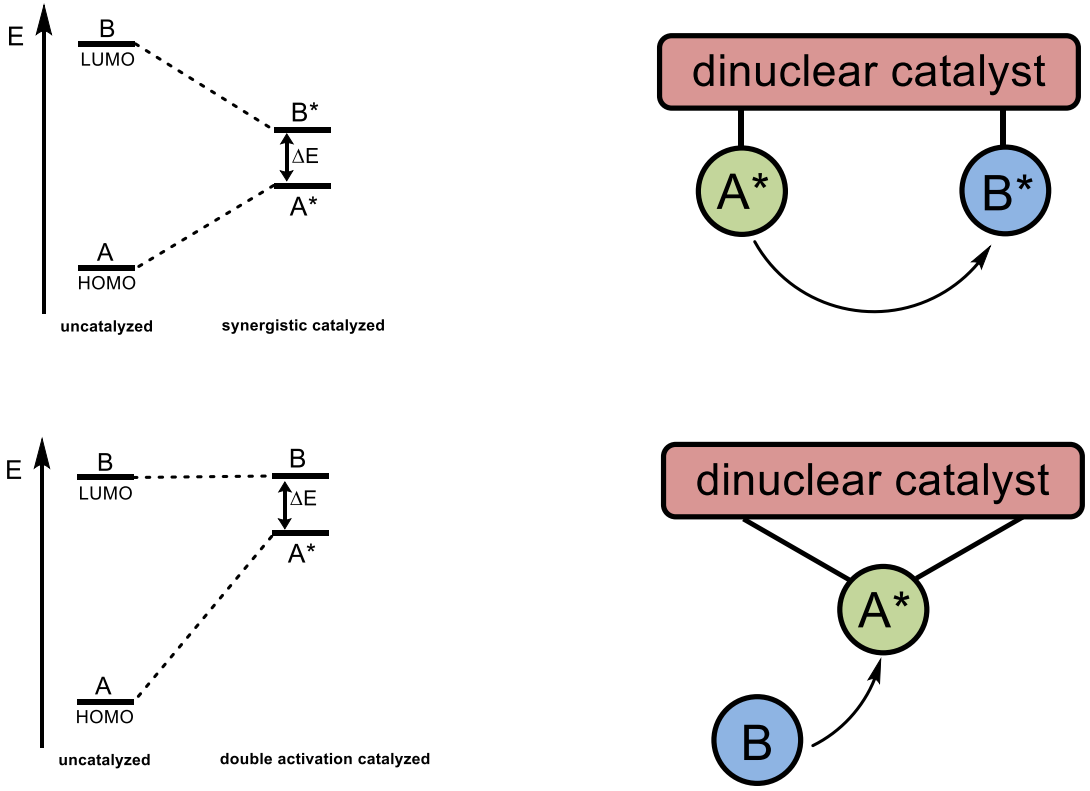


Figure 15 Schematic energy diagrams of the synergistic activation (top) and the double activation (bottom).

The general principle of cooperative catalysis is also already established in natural processes for thousands of years. It has been shown that a number of vital enzymes contain two metals in close proximity giving them outstanding properties in terms of activity and selectivity.[74] Examples therefore are oxyhemocyanin, tyrosinase (both copper-based),[75] hemerythrin, methane monooxygenase, ribonucleotide reductase (all three iron-based),[76] arginase, catalase (both manganese-based)[77] and urease (nickel-based),[78] Figure 16.

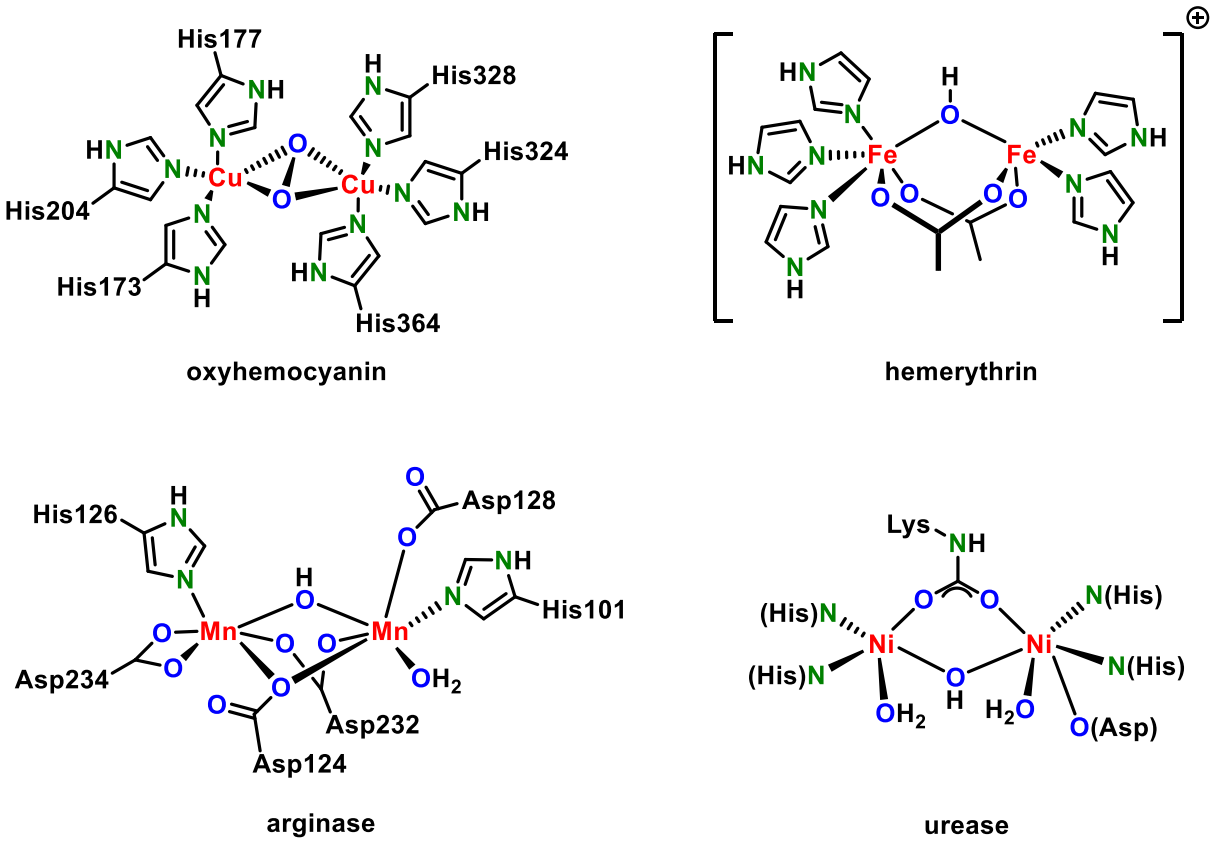
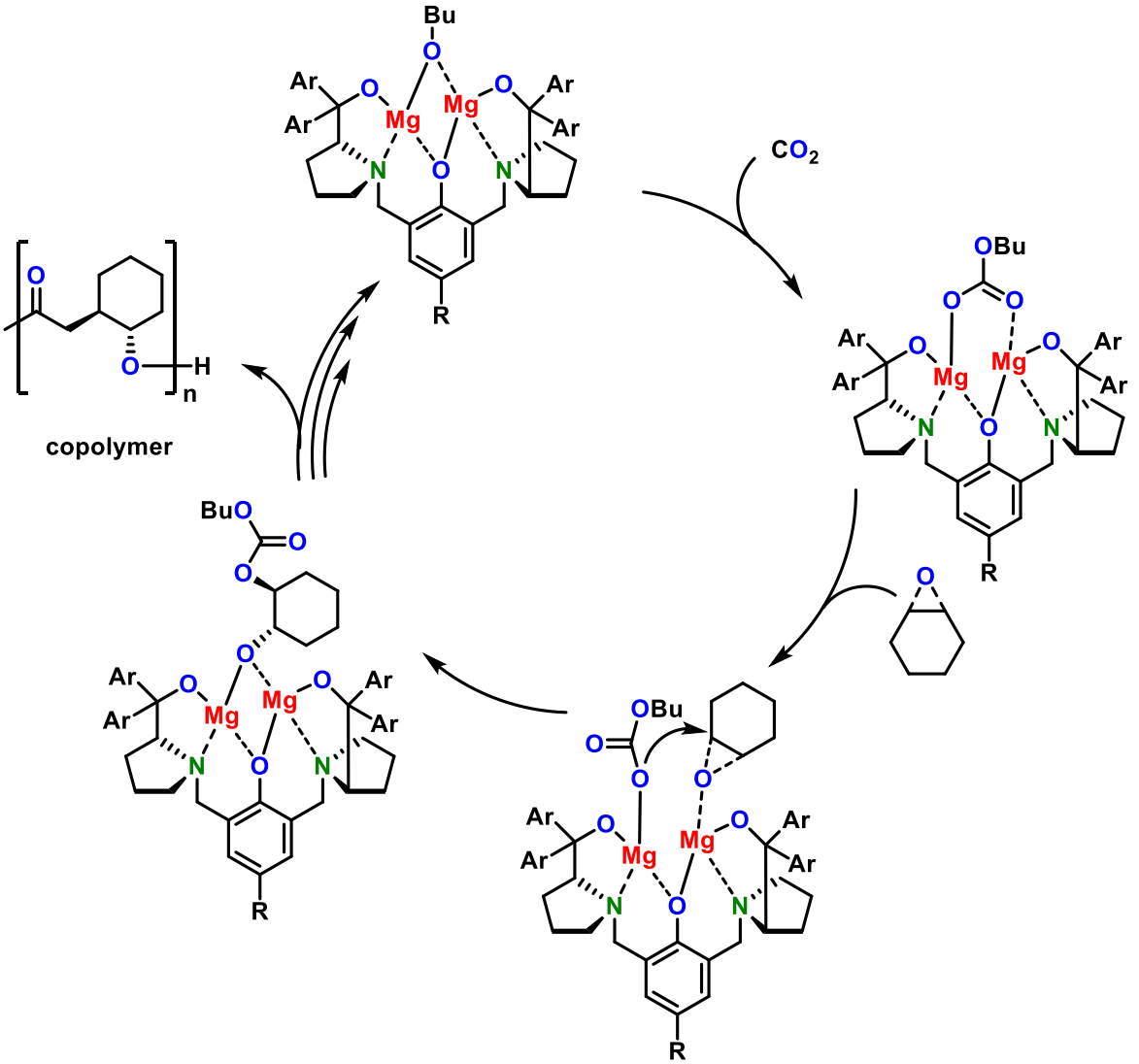


Figure 16 Active sides of oxyhemocyanin, hemerythrin, arginase and urease.

Encouraged by nature and the goal of mimicking the activity of enzymes, researches developed a multitude of dinuclear catalysts involving transition,[79] rare-earth[80] and main-group elements.[81,82] These compounds proved to be highly active in a series of organic transformations, the polymerization of olefins and the copolymerization of epoxides with CO_2.[83]

A remarkable example for a highly active and chemoselective dinuclear complex for the copolymerization of epoxides with CO_2 was published by Ding *et al.* in 2006,[82] Scheme 3. He reported a chiral, dinuclear magnesium complex based on a semi azacrown-ether ligand, which additionally exhibits the possibility of steric tunability. Besides the achievement of outstanding conversions at mild conditions (20-60 °C, 1 atm pressure of CO_2) also the employment of magnesium as metal centers is remarkable, as examples for dinuclear alkaline-earth metal catalysts remain rare.[82]



R = Me; Ar = Ph, 4-CH_3Ph, 3-CH_3Ph, 4-MeOPh, 4-Ph-Ph, 4-CF_3Ph, 3,5-$(CF_3)_2$Ph, 3,5-Me_2Ph, 4-ClPh
R = NO_2; Ar = Ph
R = ^{t}Bu; Ar = Ph
R = H; Ar = Ph

Scheme 3 Catalytic cycle for the epoxide/CO_2 copolymerization using a dinuclear magnesium complex.

1.3 References

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2. Research Objectives

During the last decades, the interest in main-group metal catalysis as environmentally benign alternative to transition metal catalysis has rapidly grown. Scientists from all over the world realized the urgency to promote resource and cost saving alternatives which led to a remarkable progress within this field of research. Even though main-group metal catalysts proved their viability on some large-scale and industrially relevant transformations, there are still processes, where they cannot reach their transition metal relatives. A promising approach to further enhance the versatility of main-group metal catalysts is therefore the synthesis of dinuclear complexes, to exploit cooperative effects between the metal centers. Whereas the chemistry of mononuclear main-group metal complexes is thoroughly explored, their dinuclear analogues are still in their infancy.

Encouraged by the auspicious results of dinuclear main-group metal compounds published so far, this work is focused on the synthesis and isolation of novel dinuclear complexes based on *N*,*N*-chelating ligands. The direct influence of the linking groups as well as the endgroups on the coordination and reaction behavior is examined. Additionally, the impact of different ligand classes and various metals on the coordination modes is a major topic throughout this work.

Therefore, the following research objectives arise:

- Synthesis and characterization of novel *N*,*N*-chelating ligands (bis(amidine)s, bis(guanidine)s and bis(amidoamine)s)
- Variation of the bridging groups and terminal endgroups of the dinucleating ligands
- Synthesis and characterization of miscellaneous magnesium based bis(amidinate)s and bis(guanidinate)s and investigation of their coordination behavior
- Synthesis and characterization of various aluminium methyl and aluminium iodide based bis(amidinate)s and bis(guanidinate)s
- Investigation of the electronic and catalytic behavior of the isolated aluminium compounds
- Synthesis and characterization of the first magnesium based bis(amidoaminate) complexes and their aluminium, tin and zinc analogues bearing various reactive groups

Preface

The following chapter has already been published in Dalton Transactions of the Royal Society of Chemistry:

'Magnesium bis(amidinate) and bis(guanidinate) complexes: impact of the ligand backbone and bridging groups on the coordination behaviour' *Dalton Trans.* **2020**, *49*, 13072.

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Author contributions

The manuscript was prepared by the first author (A. Rösch). R. Kretschmer supervised the research and revised the manuscript. All ligands (except of **2f**) and metal complexes (except of **6b)** were isolated and characterized (NMR, IR, EA, X-ray) by the first author. **2f** and **6b** were isolated by the second author S. H. F. Schreiner. VT ^{1}H NMR spectra of **4b** as well as time-dependent ^{1}H NMR spectra of **3a** were measured at the NMR Department of the University of Regensburg, for which the first author prepared the samples. All DOSY and EXSY NMR measurements were performed and evaluated at the NMR Department of the Friedrich-Schiller-Universität Jena under the supervision of P. Schüler. H. Görls evaluated the single crystal X-Ray diffraction measurements and provided the corresponding section in the Supporting Information.

Acknowledgement

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3. Magnesium bis(amidinate) and bis(guanidinate) complexes: impact of the ligand backbone and bridging groups on the coordination behavior

Abstract

A library of ten dinucleating bis(amidine) and bis(guanidine) ligands, in which the bridging groups, terminal rests, and backbone substituents were systematically altered, has been synthesized and subsequently applied in metallation reactions using three different magnesium sources. Eight Mg complexes could be isolated and fully characterized, and in seven cases their solid-state structure could be determined by means of single crystal X-ray diffraction analysis. The results evidence a versatile coordination behaviour, which ranges from the first dinuclear heteroleptic magnesium iodide complex to dinuclear homoleptic complexes. These findings indicate the crucial impact of both the ligand and the magnesium source not only on the accessibility of well-defined dinuclear complexes but also on the aggregation in solution and in the solid state.

3.1 Introduction

Over the past decades, researchers from various fields of chemistry have become more and more interested in bimetallic and dinuclear compounds, in which two active sites are framed within a single molecule.[1] These molecules often display characteristics that cannot be accessed using their mononuclear congeners, due to cooperative effects.[2] However, the efficient synthesis of homo- and heterodinuclear compounds remains challenging and is often affected by an appropriate selection of the dinucleating ligand. Among the very relevant kinds of N,N-dinucleating ligands,[3] most research studies have been devoted to

bis(amidine)s,[4] while bis(β-diketimine)s[5] and bis(guanidine)s[6] only recently received particular attention. Bis(amidinate)-based compounds have found numerous applications in materials science and catalysis,[7] and the related bimetallic complexes are associated with reactivities and selectivities that could not be achieved using their mononuclear relatives.[8] In this regard, the geometric features, *i.e.*, the metal–metal separation and the relative orientation of both active sites, and electronic aspects such as the capability of the backbone to donate or withdraw electron density, play a crucial role and may be tuned by adapting the ligand framework. While dinucleating ligands have been regularly used for the complexation of transition metals and rare earth elements, examples of complexes containing early main-group elements remain rare.[3,9] This is surprising, considering the catalytic potential of mononuclear complexes of s- and p-block metals.[10] Due to their high abundance and low toxicity, the group 2 elements magnesium and calcium are particularly attractive,[10*b,c,f,g*,11] but only a small number of related dinuclear complexes has been reported so far.[5*l*,12]

Among these, the Harder group has investigated magnesium and calcium complexes based on bis(salicylaldimine)s and bis(β-diketimine)s, respectively, possessing rigid bridging groups such as hydrazine, 1,3- and 1,4-phenylene, 2,3,5,6-tetramethyl-1,4-phenylene, and 2,6-pyridylene.[5*l*,12*b,d–f,h,i*] When using bis(salicylaldimine)s, the authors observed in the case of magnesium, dinuclear heteroleptic complexes of type **I**, while for calcium a mixture of heteroleptic and intermolecular homoleptic (type **II**) dinuclear complexes was obtained besides polymeric aggregates, Fig. 1.[5*g*,12*b*] In the case of bis(β-diketiminate)s, several heteroleptic (**I**)[5*e,g*] and homoleptic (**II**)[5*e,g*,12*e*] complexes were observed for both, calcium and magnesium, while for the latter di- (**III** and **IV**)[12*d*] and tetranuclear (**V** and **VI**)[12*h,i*] complexes were also reported, in which additional ligands such as *n*-butyl, amidoborane or hydrides act as intra- or intermolecular bridges. Notably, in the case of the 2,6-pyridylene-bridged magnesium bis(β-diketiminate) complex additional but unique binding modes were observed.[12*h*] We wondered how the coordination behaviour changes on going from the well-established bis(β-diketiminate)s to (bis(amidinate)s and bis(guanidinate)s. Hence, we synthesized the related nitrogen-bridged protio-ligands and investigated their reactivity

towards magnesium precursors; our findings are reported herein. Please note that dinuclear magnesium complexes incorporating backbone-bridged bis(amidinate)s have been reported before.[4k]

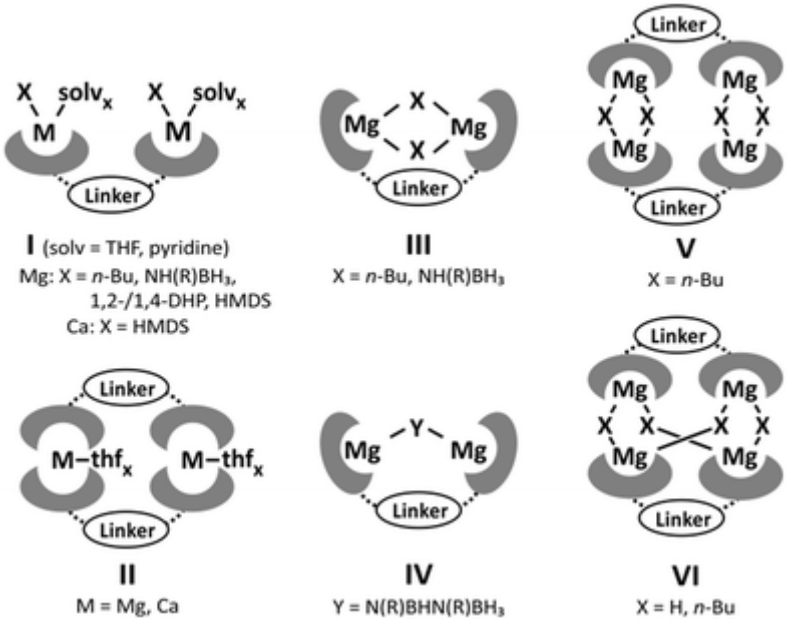


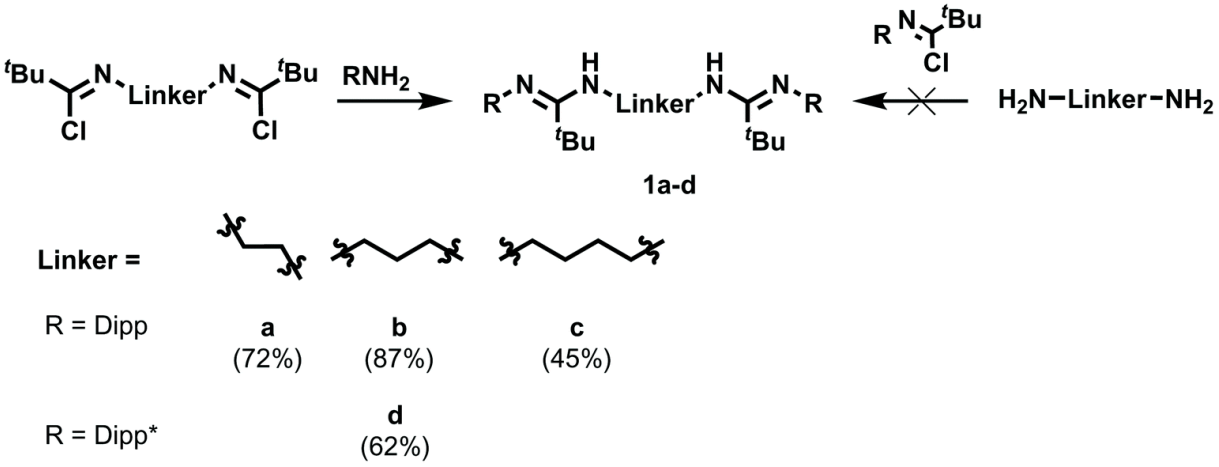
Fig. 1 Known coordination modes of calcium and magnesium bis(β-diketiminate) and bis(salicylaldiminate) complexes. DHP = dihydropyridine.

3.2 Results and discussion

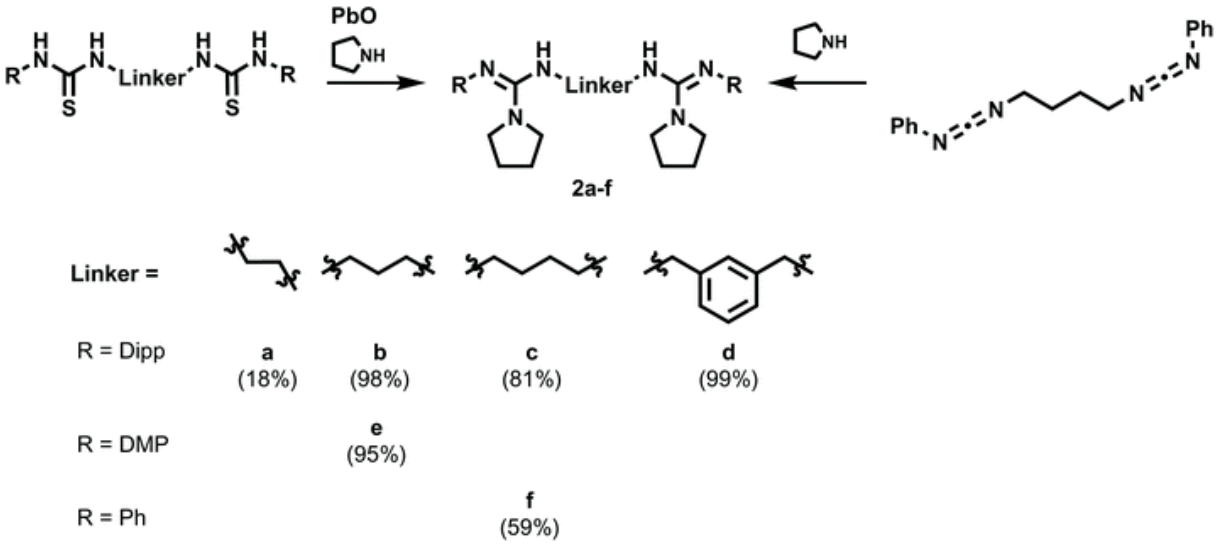
Protio-ligand synthesis

Nitrogen-bridged bis(amidine)s are generally available by various routes,[3] from which those originating from either bis(imidoylchloride)s or imidoylchlorides are most versatile. Although bis(amidine)s are also accessible starting from bis(carbodiimide)s, the instability of the latter limits the scope of the reaction. Hence, we targeted the synthesis of N-bridged bis(amidine)s **1a–d** through aminolysis of the related bis(imidoylchloride)s, Scheme 1, and also

investigated the reaction of imidoylchlorides with the primary diamines. However, only the aminolysis of bis(imidoylchloride)s allowed for the isolation of the related bis(amidine)s, **1a–d**, which are obtained in yields ranging from 45 to 87%. In contrast, treating the secondary diamines with two equivalents of imidoylchloride gave rise to complex reaction mixtures. Bis(guanidines) **2b–e** were synthesized in good to excellent yields using the one-pot procedure recently reported by us,[6h] which however gives **2a** only as a side-product in 18% yield along with the related 3,4-ethylene-bridged 1,1,2,5-tetrasubstituted biguanide.[6i] **2f** was alternatively synthesized from the related bis(carbodiimide) upon reaction with pyrrolidine, as the reaction directly originating from the respective bis(thiourea) gave a complex reaction mixture most likely due to the absence of steric protection, Scheme 2.



Scheme 1 Synthesis of bis(amidine)s **1a–d** employed in this work. Dipp = 2,6-diisopropylphenyl, Dipp* = 2,6-dibenzhydryl-4-methylphenyl.



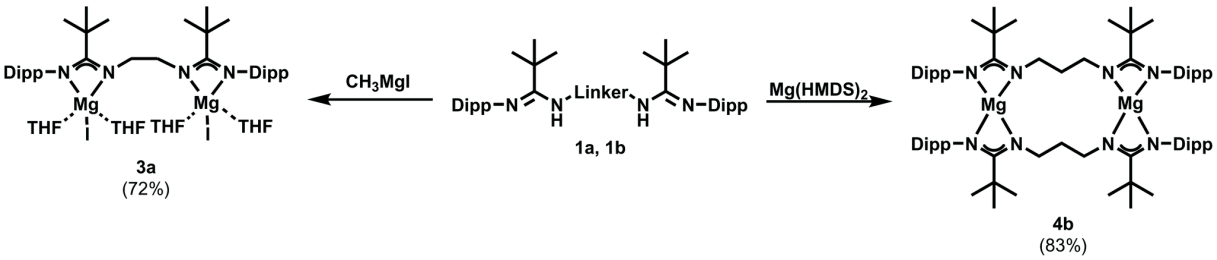
Scheme 2 Synthesis of bis(guanidines)s **2a–f** employed in this work. Dipp = 2,6-diisopropylphenyl, DMP = 2,6-dimethylphenyl.

Synthesis of mono- and dinuclear magnesium compounds

Aiming to access dinuclear magnesium bis(amidinate) and bis(guanidinate) complexes, the respective protio-ligands were treated with various magnesium reagents including magnesium bis(hexamethyldisilazide) $Mg(HMDS)_2$, di-*n*-butylmagnesium $Mg(n\text{-}Bu)_2$ as well as methylmagnesium iodide CH_3MgI. Please note that the first two have been used previously to derive magnesium bis(β-diketiminate) and bis(salicylaldiminate) complexes, while reports about the applications of CH_3MgI to derive dinuclear heteroleptic magnesium iodide complexes have no precedence in the literature.

Reacting the bis(amidine)s **1** with $Mg(HMDS)_2$ (**1a–d**), $Mg(n\text{-}Bu)_2$ (**1a** and **1d**) or CH_3MgI (**1a–d**) affords rather complex reaction mixtures as evidenced by the ^1H NMR spectra of the crude products. Despite the repeated attempts to obtain crystals under various conditions, we were only able to isolate clean products in two cases, Scheme 3. Adding a few drops of tetrahydrofuran to the crude mixture obtained from the reaction of **1a** with two equivalents of methyl magnesium iodide causes instantaneous formation of the crystalline material,

from which we were able to separate single crystals suitable for X-ray diffraction analysis. The related solid-state structure of **3a**, Fig. 2, consists of a heteroleptic dinuclear magnesium(II) iodide complex and its structural parameters are discussed further below.



Scheme 3 Synthesis of the heteroleptic (**3**) and homoleptic (**4**) bis(amidinate) complexes from the respective protio-ligands upon treatment with either methylmagnesium iodide or magnesium bis(hexamethyldisilazide). Dipp = 2,6-diisopropylphenyl.

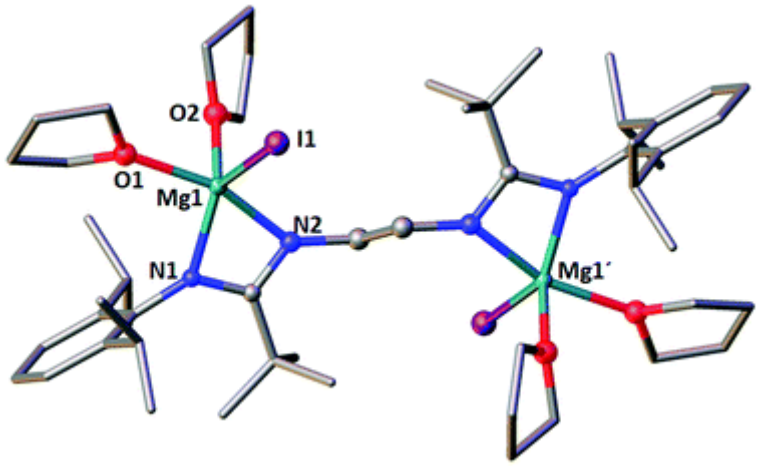
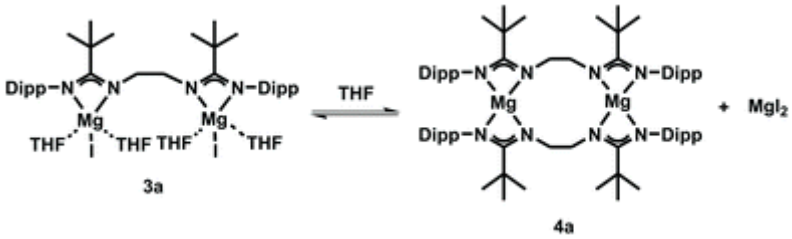


Fig. 2 Solid-state structure of **3a** (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]: Mg1–Mg1' 7.1542(13), Mg1–I1 2.7659(7), Mg1–N1 2.0733(17), Mg1–N2 2.1262(19), Mg1–O1 2.1465(16), Mg1–O2 2.0423(19), N1–Mg1–N2 63.26(7), O1–Mg1–O2 88.55(7).

Although the solubility of **3a** in benzene is rather low, a simple room temperature ^{1}H NMR spectrum, *i.e.*, one septet and two doublets corresponding to the methine and methyl resonances of the Dipp groups and an averaged singlet accounting for the four methylene protons of the bridge, is observed. The fast exchange and averaging on the NMR timescale

indicate that the heteroleptic complex persists in solution. Notably, two molecules of THF are loosely bound and readily removed in a vacuum as evidenced by the integration of the ^{1}H NMR spectrum. A simple pattern of resonances was also observed if the ^{1}H NMR spectra of the freshly prepared samples in THF-d_8 were recorded. However, over time the precipitation of the crystalline material and the appearance of new signals in the ^{1}H NMR spectrum were observed, Fig. S1. This is in good agreement with the Schlenk equilibrium that is shifted over time towards the intermolecular homoleptic complex, **4a**, Scheme 4. Time-dependent ^{1}H NMR spectra reveal a half-life of about 18 hours (0.023 mol L^{-1}) for **3a** in THF-d_8, Fig. S2. The structure of **4a** in the solid state was unambiguously confirmed by X-ray diffraction analysis, Fig. 3a.



Scheme 4 Schlenk equilibrium between **3a** and **4a**. Dipp = 2,6-diisopropylphenyl.

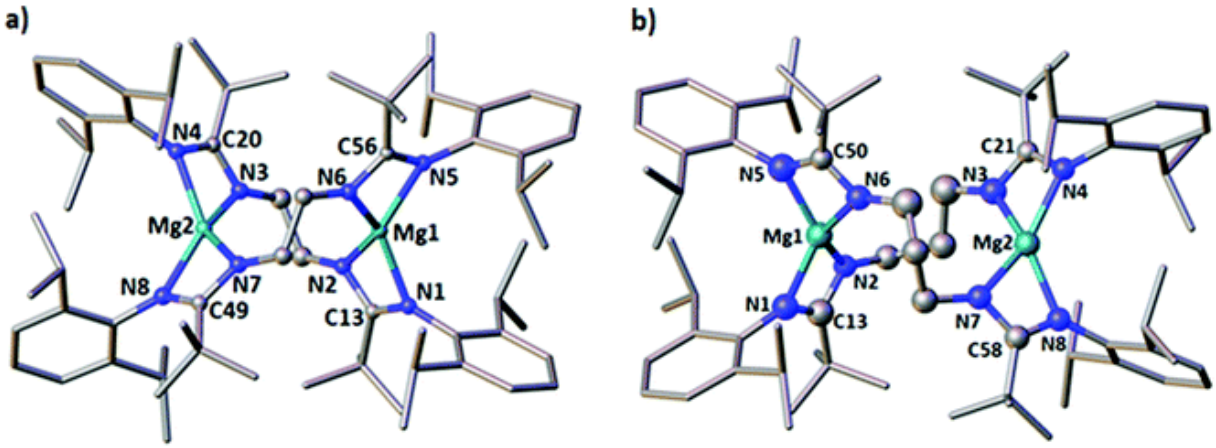


Fig. 3 Solid-state structures (hydrogen atoms and in the case of **4b** also co-crystallized toluene are omitted for the sake of clarity) with selected bond lengths [Å] and angles [°]: (a) **4a**: Mg1–Mg2 4.3350(9), Mg1–N1 2.0514(11), Mg1–N2 2.0555(12), Mg1–N5 2.0629(12), Mg1–N6 2.0361(13), Mg2–N3 2.0507(11), Mg2–N4 2.0436(10), Mg2–N7 2.0322(9), Mg2–N8 2.0569(11), N1–C13 1.3443(14), N2–C13 1.3401(14), N3–C20 1.3413(15), N4–C20 1.3385(16), N5–C56 1.3424(18), N6–C56

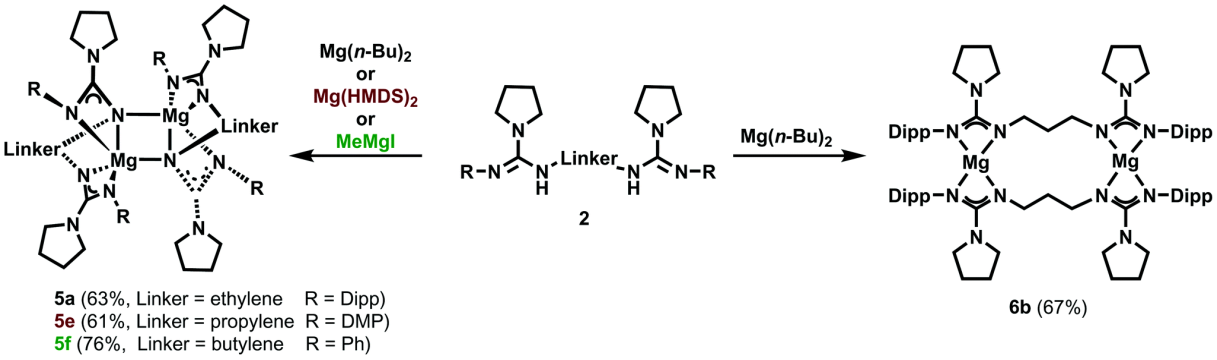
1.3412(16), N7–C49 1.3414(14), N8–C49 1.3442(12), N1–Mg1–N2 65.49(4), N5–Mg1–N6 65.46(4), N3–Mg2–N4 65.56(4), N7–Mg2–N8 65.57(4); (b) **4b**: Mg1–Mg2 5.1714(14), Mg1–N1 2.053(3), Mg1–N2 2.084(3), Mg1–N5 2.0403(19), Mg1–N6 2.055(3), Mg2–N3 2.045(3), Mg2–N4 2.060(2), Mg2–N7 2.066(3), Mg2–N8 2.0380(18), N1–C13 1.328(3), N2–C13 1.325(5), N3–C21 1.331(4), N4–C21 1.339(3), N5–C50 1.334(4), N6–C50 1.331(2), N7–C58 1.349(4), N8–C58 1.349(4), N1–Mg1–N2 63.58(13), N5–Mg1–N6 64.70(9), N3–Mg2–N4 64.83(10), N7–Mg2–N8 66.82(9).

As magnesium iodide complexes are suitable precursors to access the related dinuclear Mg(I) derivatives possessing intermolecular Mg–Mg bonds,[13] we were interested to see whether **3a** can be reduced to a low-valent derivative featuring an intra-molecular magnesium–magnesium bond. Repeated attempts to reduce **3a** using KC_8, potassium mirror, or elemental caesium in hydrocarbon solvents remained unsuccessful and gave rise to **4a**. Using more polar solvents such as THF does not appear reasonable due to the shift of the Schlenk equilibrium, as discussed before. Notably, the cyclic voltammograms recorded from the freshly prepared solutions of **3a** in THF do not reveal any reduction event above −3.30 V (against Fc/Fc^+), Fig. S13.

4b is the only other yet isolated magnesium complex incorporating a bis(amidinate), which was obtained in very good yield by reacting bis(amidine) **1b** with two equivalents of magnesium bis(hexamethyldisilazide). An X-ray diffraction analysis of the single crystals of **4b** established its molecular structure in the solid state, Fig. 3b, which will be discussed further below.

Reacting bis(guanidine)s **2** with di-*n*-butyl magnesium gave only in three cases (**2a,b,d**) well-defined species, Scheme 5, while no product could be isolated with the other protio-ligands. However, upon using $Mg(HMDS)_2$ (with **2b–e**) or CH_3MgI (with **2b–d,f**), two more products, *i.e.*, **5e** and **5f**, could be isolated. Among these five species, single crystals of **5a**, **5e**, **5f**, and **6b** suitable for X-ray diffraction analyses could be obtained after a short work-up and their molecular structures are given in Fig. 4 and 5. Although the product of the reaction of the 1,3-xylylene-bridged bis(guanidine) **2d** with di-*n*-butyl-magnesium was obtained as a

colourless solid (**7**), recrystallization attempts from various solvents as well as solvent combinations did not allow us to obtain single crystals suitable for X-ray diffraction analysis.



Scheme 5 Synthesis of the dinuclear homoleptic bis(guanidinate) magnesium complexes **5** and **6** from the respective protio-ligand **2** using various magnesium precursors. Dipp = 2,6-diisopropylphenyl and DMP = 2,6-dimethylphenyl.

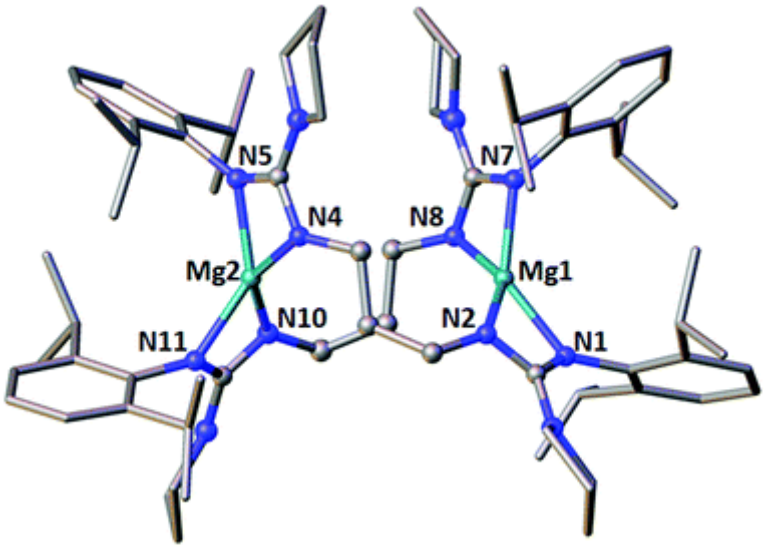


Fig. 4 Solid-state structure (hydrogen atoms are omitted for the sake of clarity) of **6b** with selected bond lengths [Å] and angles [°]: Mg1–Mg2 5.1725(8), Mg1–N1 2.0451(12), Mg1–N2 2.0363(11), Mg2–N4 2.0367(12), Mg2–N5 2.0365(13), Mg1–N7 2.0527(12), Mg1–N8 2.0301(11), Mg2–N10 2.0326(14), Mg2–N11 2.0378(12), N1–Mg1–N2 66.48(5), N4–Mg2–N5 66.77(5), N7–Mg1–N8 66.46(5), N10–Mg2–N11 66.56(5).

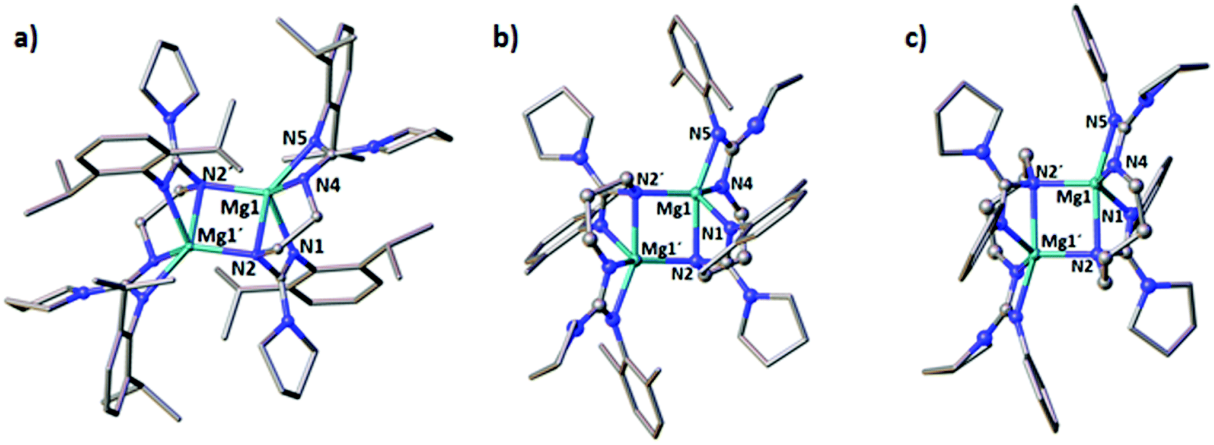


Fig. 5 Solid-state structures (hydrogen atoms and in the cases of **5a** and **5e** co-crystallized toluene are omitted for the sake of clarity) with the selected bond lengths [Å] and angles [°]: (a) **5a**: Mg1–Mg1' 3.0348(8), Mg1–N1 2.1541(11), Mg1–N2 2.2703(11), Mg1–N4 2.0646(13), Mg1–N5 2.1521(12), Mg1–N2' 2.0736(12), N1–Mg1–N2 62.05(4), N4–Mg1–N5 64.29(4), N2'–Mg1–N2 91.48(4); (b) **5e**: Mg1–Mg1' 2.9929(8), Mg1–N1 2.1005(14), Mg1–N2 2.2336(14), Mg1–N4 2.0604(11), Mg1–N5 2.1298(13), Mg1–N2' 2.0949(11), N1–Mg1–N2 62.95(5), N4–Mg1–N5 64.47(5), N2'–Mg1–N2 92.57(5); (c) **5f**: Mg1–Mg1' 3.0823(10), Mg1–N1 2.0789(12), Mg1–N2 2.2913(12), Mg1–N4 2.0897(13), Mg1–N5 2.1366(13), Mg1–N2' 2.1276(13), N1–Mg1–N2 61.94(5), N4–Mg1–N5 64.34(5), N2'–Mg1–N2 91.62(5).

Solid-state structures

The heteroleptic bis(amidinate) complex, **3a**, Fig. 2, possesses two equivalent magnesium(II) centres that are each penta-coordinated to one N,N-chelating amidinate unit, an iodide ligand, and two molecules of THF. In the case of the two homoleptic bis(amidinate) complexes, **4a** and **4b**, Fig. 3, each of the two magnesium ions is four-fold coordinated by two N,N-chelating amidinate units, which belong to two different bis(amidinate) ligands. The Mg–N bond lengths (2.0733(17)–2.1262(19) Å) and the N–Mg–N bite angle (63.26(7)°) within **3a** are comparable to those of the only yet reported mononuclear amidinate magnesium iodide complex[14] (Mg–N 2.085(6) and 2.140(6) Å; N–Mg–N 64.3(2)°). The corresponding Mg–N bond lengths within **4a** and **4b** are slightly shorter and range from 2.0322(9) to 2.084(3) Å, consistent with values previously reported for mononuclear homoleptic magnesium amidinate complexes (2.039(3) to 2.079(18) Å).[15] The same holds true for the N–Mg–N

angles that fall in between 63.58(13)° and 66.82(9)°, Table 1. The nitrogen–carbon bond lengths of the amidinate backbone (1.323(3)–1.352(2) Å) are almost equal in all three cases indicating the delocalized nitrogen–carbon bonding. Notably, the Mg–I bond length of 2.7659(7) Å within **3a** resembles the value of the related mononuclear complex (2.783(2) Å).

Table 1 Selected bond lengths [Å] and angles [°] of the mono- and dinuclear magnesium bis(amidinate) and bis(guanidinate) complexes.

Compound	Mg–Mg	Mg–N	N–Mg–N
3a	7.1542(13)	2.0733(17)–2.1262(19)	63.26(7)
4a	4.3350(9)	2.0322(9)–2.0629(13)	65.46(4)–65.57(4)
4b	5.1714(14)	2.0380(18)–2.084(3)	63.58(13)–66.82(9)
5a	3.0348(8)	2.0646(13)–2.2703(11)	62.05(4)–91.48(4)
5e	2.9929(8)	2.0604(11)–2.2336(14)	62.95(5)–92.57(5)
5f	3.0823(10)	2.0789(12)–2.2913(12)	61.94(5)–91.62(5)
6b	5.1725(8)	2.0301(11)–2.0527(12)	66.46(5)–66.77(5)

The dinuclear complex **6b** is reminiscent of **4b**, but the two magnesium ions are each framed by two N,N-chelating guanidinate units of two bis(guanidinate) ligands. The magnesium–nitrogen bond lengths within **6b** are comparable to those in **4b**, but the N–Mg–N guanidinate bite angles are more obtuse than those of their amidinate relatives.

While the values discussed before remain largely unaffected by varying the linker group, the metal–metal separation increases on going from **4a** (4.3350(9) Å) to **4b** (5.1714(14) Å) and **6b** (5.1725(8) Å), respectively, as a result of the additional CH_2 group of the bridge. The separation is even further increased in the case of **3a** (7.1542(13) Å) due to the opposing orientation of the two magnesium centres. The shorter ethylene bridge confines the overall

flexibility of **4a**, and the angles between the two MgNCN metallacycle planes of each magnesium ion, which are inclined by 77.4° and 79.4°, are more obtuse than those of **4b**, with values of 67.6° and 77.7°. However, in the case of **6b**, the angles between the two MgNCN metallacycles are closer to orthogonality (78.3° and 81.4°) as compared to those of **4b**. Notably, in both cases, these angles are moved towards orthogonality compared to those reported for related mononuclear amidinate and guanidinate complexes (54°–80°).[15b,c,16]

The homoleptic complexes **5a**, **5e**, and **5f** crystallize as centrosymmetric dimers consisting of two mononuclear homoleptic magnesium bis(guanidinate) fragments, Fig. 4. Hence, each magnesium ion possesses a coordination number of five and comprises four magnesium–nitrogen bonds to the chelating bis(guanidinate) and an additional intermolecular Mg–N bond to a lateral nitrogen atom of one of the guanidine units. Thus, a primary transoid ladder[17] of *i* or S_2 symmetry with a central four-membered Mg_2N_2-ring is formed and the two guanidinate units of each ligand are unequally bonded in a μ-1'κ^1N^2:1$\kappa^2N^1N^2$ and 1κ^2N^4,N^5 fashion, respectively. While the overall coordination mode has no precedence in the literature for any metallated nitrogen-based ditopic ligand,[3] it is reminiscent of the dimeric calcium and magnesium complexes based on guanidinate and amidinate ligands reported before by the groups of Hill and Winter.[18] The bond distances between the magnesium and the terminal nitrogen atoms, *i.e.*, Mg–N1 and Mg–N5, are longer (2.0789(12)–2.1541(11) Å) compared to the values of 2.040(3) to 2.052(2) Å reported for homoleptic mononuclear guanidinate complexes.[16,19] However, the non-bridging Mg–N4 interactions (2.0604(11)–2.0897(13) Å) resemble these values, while the bonding between the magnesium and the lateral bridging nitrogen atoms, *i.e.*, Mg–N2, is significantly affected by the bridging interaction as expressed by significantly longer bond distances of 2.2336(14) to 2.2913(12) Å. The intermolecular Mg–N2' and Mg'–N2 bond lengths increase on going from **5a** (2.0736(12) Å) to **5e** (2.0949(11) Å) to **5f** (2.1276(13) Å), which might be either due to the increasing length of the linker group or due to a decrease in the dispersive interaction upon reducing

the bulkiness of the terminal aryl substituent. The magnesium–magnesium separation, finally, amounts to 3.0348(8) (**5a**), 2.9929(8) (**5e**), and 3.0823(10) Å (**5f**). The bite angles of the non-bridging guanidinate units are more acute (61.94(5)–62.95(5)°) as compared to those of the bridging ones (64.29(4)–64.47(5)°) and closer to those of the mononuclear guanidinate complexes with values between 65.90(10) and 66.67(10)°.[16,19]

Behavior in solution

As discussed before, **3a** resembles an averaged ^{1}H NMR spectrum at room temperature, but on going from **3a** to **4a**, the rotation about the C–C bond of the ethylene bridge is effectively cancelled out and the respective methylene protons become inequivalent causing the appearance of two multiplets instead of one singlet in the ^{1}H NMR spectrum (C_6D_6), Table 2. Furthermore, two multiplets and three doublets (ratio 1 : 2 : 1) for the respective methine and methyl proton resonances of the 2,6-diisopropylphenyl substituents are observed. In contrast to the well-resolved room-temperature ^{1}H NMR spectrum of **4a**, the respective spectrum of **4b** contains a multiplet and a number of broadened resonances, which likely arise from the slow conformational exchange of the complex on the NMR timescale due to the more flexible propylene bridge. Upon cooling to 193 K, these resonances shifted slightly but did not resolve into separate peaks, Fig. S3. However, in the case of **6b**, the bis(guanidinate) relative of **4b**, well-resolved ^{1}H and ^{13}C NMR spectra were obtained and the pattern of the resonances for the Dipp groups, *i.e.*, four methyl doublets and two methine septets, is in good agreement with the solid-state structure.

Table 2 ^{1}H NMR shift [ppm] of the mono- and dinuclear magnesium bis(amidinate) and bis(guanidinate) complexes.

Compound (solvent)	**CH(C*H*$_3$)$_2$**	**C*H*(CH$_3$)$_2$**	**Linker**
3a (C_6D_6)	d (1.28), m (1.35–1.37)	m (3.58–3.65)	s (4.11)
3a (THF-d_8)	d (1.16), d (1.25)	sept (3.45)	s (3.79)
4a (C_6D_6)	d (0.43), m (1.24–1.26), d (1.35)	sept (3.16), m (3.50–3.54)	m (3.50–3.54), m (4.45–4.50)
4b (THF-d_8)	m (1.07–1.21)	br s (3.13–3.31)	m (1.92–2.09), m (3.62–3.74)
5a (C_6D_6/THF-d_8)	dd (1.20)	sept (3.21)	m (3.14–3.16)
6b (C_6D_6)	d (0.54), d (1.16)	m (3.06–3.13), m (3.89–3.96)	m (2.34–2.41), m (3.45–3.52), m (3.61–3.67)
7 (C_6D_6)	m (1.07–1.13), d (1.28)	m (3.50–3.64)	s (4.36), m (7.30–7.56)
7 (toluene-d_8)	br (1.00), d (1.25)	br (3.51)	s (4.30), m (6.98–7.45)

The ^{1}H NMR spectra of **5a**, **5e**, and **5f** are consequently affected by the NMR solvent. The low solubility of **5a** in apolar solvents necessitates the use of THF-d_8 at least as a co-solvent. One septet and two doublets in the respective ^{1}H NMR spectrum account for the Dipp isopropyl groups indicating the conformational averaging on the NMR timescale. The increased solubility of **5e** allows obtaining the ^{1}H NMR spectra in both toluene-d_8 and THF-d_8. In the first case, the methyl groups within **5e** appear as four singlets evidencing that the complex is not symmetrical in solution. In THF-d_8, two singlet resonances are observed, which indicates a higher symmetry likely due to the coordination of THF-d_8 to the magnesium centre. **5f** does not contain a valuable ^{1}H NMR probe as in the cases of **5a** and **5e**, but shows only broadened resonances for the protons of the linker group and the backbone-based pyrrolidine unit.

Finally, the room temperature ^{1}H NMR spectrum of **7** in deuterated benzene or toluene-d_8 includes one doublet and one broadened resonance for the Dipp methyl groups and one broad resonance for the respective methine proton, which indicates a symmetric or averaged structure in solution. Adding about 20 equivalents of THF to this solution does not significantly affect the spectrum but the dissolution of **7** in THF-d_8 gives a significantly more complex pattern of resonances with partially overlapping signal groups, which impedes a distinct assignment, Fig. S4–S8.

To gain further insight into the behaviour in solution, diffusion-ordered NMR spectroscopy (DOSY) experiments have been conducted for **4b**, **5e**, **5f**, and **7** using tetrakis(trimethylsilyl)silane as an internal reference, Table 3. In the case of **4b**, the experimentally obtained diffusion coefficient (D = 5.52 × 10^{-10} m^2 s^{-1}) reveals an experimental molecular weight of 1225 g mol^{-1} when assuming highly compact spheres, which is close to the calculated value of 1166.41 g mol^{-1}. In the case of **5e**, the impact of the NMR solvent on the aggregation has been probed with both, C_6D_6 and THF-d_8, but the same diffusion coefficient (D = 7.75 × 10^{-10} m^2 s^{-1}) and hence molecular weight (536 g mol^{-1}) were observed. This indicates the presence of a monomeric species (a molecular weight of 496.99 and 577.14 g mol^{-1} without and with considering a coordinated THF-d_8 molecule, respectively) in contrast to the solid-state dimer. The same holds true for **5f** (D = 1.2 × 10^{-9} m^2 s^{-1}) for which the experimental molecular weight of 546 g mol^{-1} is in good agreement with the calculated value of 535.06 g mol^{-1} assuming one coordinated molecule of THF-d_8.

Table 3 Experimental values of the DOSY experiments.

Compound (solvent)	Diffusion coefficient	Calc. mol weight
4b (THF-d_8)	5.52×10^{-10}	1225
5e (toluene-d_8)	7.75×10^{-10}	536
5e (THF-d_8)	7.75×10^{-10}	536
5f (THF-d_8)	1.12×10^{-9}	546
7 (THF-d_8)	5.20×10^{-10}	1045
7 (toluene-d_8)	4.25×10^{-10}	1255

As mentioned before, the behaviour of compound **7** in solution is strongly solvent dependent and so are the experimentally determined diffusion coefficients: in the case of toluene-d_8, only one major component was observed and the diffusion coefficient (D = 4.25 × 10^{-10} m^2 s^{-1}) corresponds to a molecular weight of 1255 g mol^{-1}. Notably, a comparable value is observed when about 20 equivalents of THF are added. These findings indicate that **7** either resembles a structure comparable to that of complex **4** or exists as a dimeric aggregate as observed for the complexes **5** in the solid state. In both cases, the calculated molecular weight amounts to 1342.6 g mol^{-1}. In THF-d_8, two similar species with a diffusion coefficient of about 5.2 × 10^{-10} m^2 s^{-1} and a molecular weight of 1045 g mol^{-1} were observed. This number does not match that of either a mono- or a dinuclear complex but falls well in between the values of the two species (average molecular mass 1046 g mol^{-1}), Fig. 6. Please note that depending on the exchange rate, converging and even averaging diffusion coefficients have been reported,[20] which further indicates a THF-dependent equilibrium between the mono- and dinuclear complexes. Indeed, the ^{1}H exchange spectroscopy (EXSY) experiments using a mixing time of 1 s revealed distinct cross-peaks indicating chemical exchange at room temperature, Fig. S9–S12.

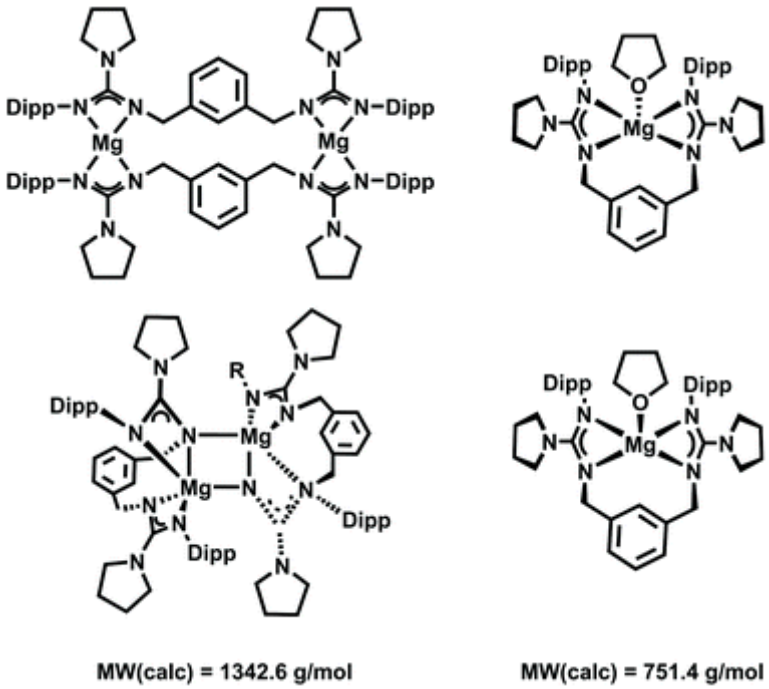


Fig. 6 Conceivable structures of the solution of complex **7**.

3.3 Conclusion

The application of four bis(amidine) and six bis(guanidine) ligands allowed for the synthesis of overall eight magnesium complexes possessing different coordination modes. The results illustrate how crucially the electronic and steric features of the dinucleating ligand on the one hand and the metal source on the other affect the complex formation and the related coordination behaviour. Only in one case, *i.e.*, upon using ethylene-bridged bis(amidine) along with CH_3MgI, a heteroleptic magnesium iodide complex could be obtained. However, while complex **3a** is stable in hydrocarbon solutions, the dissolution in THF shifts the Schlenk equilibrium and gives rise to the respective dinuclear homoleptic complex **4a**. Such a kind of complex was also observed in the cases of propylene-bridged bis(amidinate) **4b** and the bis(guanidinate) **6b**, which share comparable structural features indicating a negligible

impact of the backbone substituent. Furthermore, the bis(guanidine)s, **2a**, **2e**, and **2f**, possessing various linker groups and terminal substituents afford intramolecular homoleptic complexes that form dimers in the solid state. Overall, and due to the Schlenk equilibrium, bis(amidinate)s and bis(guanidinate)s containing flexible linker groups appear to be not very suitable for deriving heteroleptic dinuclear magnesium complexes, which could be used as ligands for other metal(loid)s or adopted for further applications in catalysis.

3.4 References

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3.5 Supporting information

General

All inorganic 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 removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally through P_4O_{10}. Toluene, THF, dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS- 800). D_6-Benzene and d_8-toluene were used as p.a. grade and were distilled from Na/benzophenone prior to use. THF-d_8 was used without further purification. $CDCl_3$ was dried by distillation from calcium hydride.

2,6-dimethylphenyl isothiocyanate, phenyl isothiocyanate, pyrrolidine, 1,3-diamino propane, 1,4-diamino butane, triethyl amine, triphenyl phosphane**,** lead(II)oxide, pivaloylchloride, PCl_5, ethylenediamine and 2,6-diisopropylaniline were purchased from Sigma Aldrich.
The bis(guanidines) (1Z,1'Z)-N,N''-(ethane-1,2-diyl)bis(N'-(2,6-diisopropylphenyl)pyrrolidine-1-carboximidamide) (2a)[S1] , (1Z,1'Z)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-diisopropyl-phenyl)pyrrolidine-1-carboximidamide) (2b)[S2], (1Z,1'Z)-N,N''-(1,3-phenylene-bis(methylene))-bis(N'-(2,6-diisopropylphenyl)pyrrolidine-1-carboximidamide) (2d)[S2] and the starting material 2,6-dibenzhydryl-4-methylaniline[S3] were prepared according to published procedures.
Characterization. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CDCl_3$: δ(^1H) = 7.26), (C_6D_6: δ(^1H) = 7.16), (THF-d_8: δ(^1H) = 1.72 and 3.58) or (toluene-d_8: δ(^1H) = 2.08, 6.97, 7.01 and 7.09) and the solvent peak ($CDCl_3$: δ(^{13}C) = 77.16), (C_6D_6: δ(^{13}C) = 128.06) and (THF-d_8: δ(^{13}C) = 67.2 and 25.3), respectively. DOSY NMR spectra were measured using the *ledbpg2s* pulse

sequence for room temperature or the convection compensated *dstebpgp3s* pulse sequence at higher temperatures (D = 75 ms). Molecular weights were calculated using the ECC-DOSY method[S4] and $Si(SiMe_3)_4$ as internal standard. ASAP-HSQC-DEPT was measured using the pulse sequence of Luy *et al.*.[S5] 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.

Protio ligand synthesis

Synthesis of N,N'-(ethane-1,2-diyl)bis(2,2-dimethylpropanamide):

N,N'-(ethane-1,2-diyl)bis(2,2-dimethylpropanamide) was synthesized according to the literature procedure of O'Dea *et al.*.[S6]

Synthesis of N,N'-(propane-1,3-diyl)bis(2,2-dimethylpropanamide):

N,N'-(propane-1,3-diyl)bis(2,2-dimethylpropanamide) was synthesized according to the literature procedure of Burton *et al.*.[S7]

Synthesis of N,N'-(butane-1,4-dyl)bis(2,2-dimethylpropanamide):

A solution of pivaloylchloride (28.9 g, 240 mmol) in dichloromethane (60 mL) was added dropwise to a solution of 1,4-diaminobutane (10.6 g, 120 mmol) and trimethylamine (24.3 g, 240 mmol) in dichloromethane (400 mL). After stirring for 20 h at room temperature and 4 h under reflux, water (300 mL) was added to the white suspension giving a colorless biphasic system. The organic phase was separated and washed with water (300 mL) and brine (200 mL). The product was dried over Na_2SO_4 and the solvent was removed *en vacuo* yielding

N,N'-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) (15.8 g, 62.0 mmol 51%.) in analytically pure form as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.16 (s, 18 H, C(CH_3)$_3$), 1.49 (quint, *J* = 6.0 Hz, 4 H, CH_2(CH_2)$_2$$CH_2$), 3.23 (dt, *J* = 6.0 Hz, 4 H, CH_2(CH_2)$_2$$CH_2$), 6.00 (s, 2H, N*H*). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.0 (CH_2(CH_2)$_2$$CH_2$), 27.6 (($CH_3$)$_3$C), 38.7 (($CH_3$)$_3$*C)*, 39.0 ($CH_2$($CH_2$)$_2$$CH_2$), 178.7 (($CH_3$)$_3$*C*C(O)NH).

Synthesis of (1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride):

(1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride) was synthesized according to the literature procedure of O'Dea *et al.*.[S6]

Sythesis of (1Z,1'Z)-N',N''-(propane-1,3-diyl)Bis(2,2-dimethylpropanimidoyl chloride):

Phosphorus pentachloride (43.9 g, 214 mmol) was added portionwise to a stirred solution of *N,N'*-(propane-1,3-diyl)bis(2,2-dimethylpropanamide) (25.9 g, 107 mmol) in toluene (500 mL). The reaction mixture was stirred at 100 °C for three days giving a yellow solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (29.2 g, 105 mmol, 98 %) in analytically pure form as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.26 (s, 18 H, C(CH_3)$_3$), 1.91 (quint, *J* = 6.7 Hz, 2 H, $CH_2$$CH_2$$CH_2$), 3.53 (t, *J* = 6.7 Hz, 4 H, $CH_2$$CH_2$$CH_2$). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 28.5 ((CH_3)$_3$C), 29.6 (CH_2(CH_2)CH_2), 43.7 ((CH_3)$_3$*C)*, 50.9 (CH_2(CH_2)CH_2), 153.0 ((CH_3)$_3$*C*C(Cl)N).

Synthesis of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride):

Phosphorus pentachloride (25.8 g, 124 mmol) was added portionwise to a stirred solution of *N,N'*-(butane-1,4-dyl)bis(2,2-dimethylpropanamide) (15.8 g, 62.0 mmol) in toluene (300 mL).

The reaction mixture was stirred at 100 °C for four days giving a brown solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) (8.09 g, 28.0 mmol, 45 %) in analytically pure form as a pale brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.24 (s, 18 H, C(CH_3)$_3$), 1.66 (quint, *J* = 3.0 Hz, 2 H, CH_2(CH_2)$_2$$CH_2$), 3.48 (t, *J* = 3.0 Hz, 4 H, CH_2(CH_2)$_2$$CH_2$). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.5 ((CH_3)$_3$C), 28.5 (CH_2(CH_2)$_2$$CH_2$), 43.6 (($CH_3$)$_3$*C*), 52.9 ($CH_2$($CH_2$)$_2$$CH_2$), 152.3 (($CH_3$)$_3$C*C*(Cl)N).

Synthesis of (1E,1'E)-N',N'''-(ethane-1,2-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (1a):

2,6-diisopropylamine (16.5 mL, 87.4 mmol) was added to a stirred solution of (1Z,1'Z)-N',N''-(ethane-1,2-diyl)bis(2,2-dimethylpropanimidoyl chloride) (11.6 g, 43.7 mmol) in toluene (200 mL) and the reaction was heated to reflux for three days. After cooling to room temperature the solvent was removed and the resulting solid was dissolved in a mixture of Et_2O (200 mL) and saturated Na_2CO_3 (aq.) (200 mL). The aqueous phase was extracted with Et_2O, the combined organic phases were further washed with water (5x50 mL) followed by drying over Mg_2SO_4. Solvent removal and recrystallization from MeCN gave **1a** (17.2 g, 31.5 mmol, 72 %) as a white crystalline solid.

^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 1.18 – 1.13 (m, 24H, CH(CH_3)$_2$), 1.25 (s, 18H, C(CH_3)$_3$), 2.47 (s, 4H, CH_2CH_2), 2.88 (sept, *J* = 6.8 Hz, 4H, CH(CH_3)$_2$), 3.99 (s, 2H, NH), 6.90 – 6.85 (m, 2H, *p*-C_6H_3), 6.97 (d, *J* = 7.5 Hz, 4H, *m*-C_6H_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 22.5 (CH(CH_3)$_2$), 23.1 (CH(CH_3)$_2$), 28.5 (CH(CH_3)$_2$), 29.2 (C(CH_3)$_3$), 38.8 (C(CH_3)$_3$), 43.4 (CH_2CH_2), 121.2 (*m*-C_6H_3), 122.1 (*p*-C_6H_3), 137.1 (*o*-C_6H_3), 146.1 (*i*-C_6H_3), 156.8 (NC(C(CH_3)$_3$)N). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3445 (w), 3431 (m), 2961 (m), 2869 (w), 1623 (s), 1512 (s), 1428 (s), 1217 (s), 772 (s), 720 (m). HRMS (ESI-TOF): [M + H]+ for m/z $C_{36}H_{58}N_4$ 546.4661 found 546.4695.

Synthesis of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (1b):

A solution of 2,6-diisopropylaniline (37.2 g, 210 mmol) in toluene (60 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (29.2 g, 105 mmol) in toluene (400 mL). The reaction mixture was refluxed for two days giving a white suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving an off white waxy solid. The raw product was suspended in ethylacetate (800 mL) and stirred with a saturated solution of sodium carbonate (800 mL) over 1 h giving a clear pale yellow organic phase and a colorless aqueous phase. The organic phase was separated and dried over sodium sulfate. The solvent was removed giving a brownish oil. Excessive 2,6-diisopropylaniline was removed *en vacuo* at 150 °C yielding **1b** (51.5 g, 92.0 mmol, 87 %) in analytically pure form as a pale brown waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.14, (d *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.15, (d, *J* = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.15 (bquint, 2 H, $CH_2CH_2CH_2$), 1.24 (s, 18 H, C(C*H*$_3$)$_3$), 2.45 (dt, *J* = 5.6 Hz, 6.8 Hz, 4 H, C*H*$_2$CH$_2$C*H*$_2$), 2.91(sept, *J* = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 3.98 (t, *J* = 5.6 Hz, 2H, N*H*), 6.86 (dd, *J* = 7.1 Hz, 8.2 Hz, 2 H, *p*-C$_6$*H*$_3$), 6.95 (d, *J* = 7.1 Hz, 4 H, *m*-C$_6$*H*$_3$). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.5 (CH(*C*H$_3$)$_2$), 23.1 (CH(*C*H$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 29.1 (C(*C*H$_3$)$_3$), 31.5 (CH$_2$(*C*H$_2$)CH$_2$), 38.6 (*C*(CH$_3$)$_3$), 41.0 (*C*H$_2$(CH$_2$)*C*H$_2$), 121.1 (*m*-*C*$_6$H$_3$), 121.9 (*p*-*C*$_6$H$_3$), 137.1 (*o*-*C*$_6$H$_3$), 146.2 (*i*-*C*$_6$H$_3$), 156.8 (N*C*(C(CH$_3$)$_3$)N). IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3412 (w), 2958 (m), 2871 (w), 1652 (vs), 1589 (w), 1510 (m), 1464 (m), 1430 (s), 1219 (m), 789 (m), 743 (m), 728 (w). HR MS (ESI-TOF): [M + H]+ for m/z $C_{37}H_{60}N_4$ 561.4896, found 561.4875.

Synthesis of (1Z,1'Z)-N',N''-(butane-1,4-diyl)bis(N-(2,6-diisopropylphenyl)-2,2-dimethylpropanimidamide) (1c):

A solution of 2,6-diisopropylaniline (9.82 g, 55.4 mmol) in toluene (20 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(butane-1,4-diyl)bis(2,2-dimethylpropanimidoyl chloride) (8.09 g, 27.7 mmol) in toluene (100 mL). The reaction mixture was refluxed for two days

giving a white suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving an off-white waxy solid. The raw product was suspended in ethylacetate (300 mL) and stirred with a saturated sodium carbonate solution (500 mL) over 1 h giving a clear pale yellow organic phase and a colorless aqueous phase. The organic phase was separated and dried over Na_2SO_4. The solvent was removed giving a pale brown oil, which was recrystallized from ethanol yielding **1c** (7.16 g, 12.4 mmol, 45%) in analytically pure form as a white crystalline solid.

^{1}H NMR(400 MHz, $CDCl_3$): *δ(ppm)* = 0.96 (quint, 4 H, $CH_2(CH_2)_2CH_2$), 1.13 (d, *J* = 6.9 Hz, 12 H, $CH(CH_3)_2$), 1.14 (d, *J* = 6.9 Hz, 12 H, $CH(CH_3)_2$), 1.28 (s, 18 H, $C(CH_3)_3$), 2.49 (bt, *J* = 5.1 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 2.92 (sept, J = 6.9 Hz, 4 H, $CH(CH_3)_2$), 4.02 (t, J = 5.1 Hz, 2H, NH), 6.86 (dd, *J* = 7.6 Hz, 2 H, *p*-C_6H_3), 6.96 (d, *J* = 7.6 Hz, 4 H, *m*-C_6H_3). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.6 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 28.2 ($CH_2(CH_2)_2CH_2$), 28.4 ($C(CH_3)_3$), 29.2 ($CH(CH_3)_2$), 38.6 ($C(CH_3)_3$), 43.0 ($CH_2(CH_2)_2CH_2$), 121.1 (*m*-C_6H_3), 122.1 (*p*-C_6H_3), 137.3 (*o*-C_6H_3), 146.4 (*i*-C_6H_3), 157.1 ($NC(C(CH_3)_3)N$). IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3420 (m), 2958 (m), 2869 (w), 1649 (s), 1525 (m), 1429 (m), 1192 (m), 781 (m), 746 (m), 728 (m). HR MS (ESI-TOF): [M + H]+ for m/z $C_{38}H_{62}N_4$ 575.5052, found 575.5043.

Synthesis of (1E,1'E)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-dibenzhydryl-4-methyl-phenyl)-2,2-dimethylpropanimidamide) (1d):

A solution of 2,6-dibenzhydryl-4-methylaniline (10.1 g, 22.9 mmol) in toluene (50 mL) was added to a stirred solution of (1Z,1'Z)-N',N''-(propane-1,3-diyl)bis(2,2-dimethylpropanimidoyl chloride) (3.20 g, 11.5 mmol) in toluene (200 mL) followed by stirring at reflux for two days. The solvent was removed and the yellow solid was suspended in a mixture of EtOAc (200 mL) and Na_2CO_3 (aq., saturated, 200 mL) followed by further stirring for one hour. The organic phase was separated, dried over $MgSO_4$ and the resulting yellow oil was recrystallized from MeCN to obtain **1d** (7.73 g, 7.12 mmol, 62%) as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$)*: δ (ppm)* = -0.75 (quint, *J* = 5.0 Hz ,2H, $CH_2CH_2CH_2$), 1.12-1.16 (m, 4H, $CH_2CH_2CH_2$), 1.16 (s, 18H, $C(CH_3)_3$), 2.25 (s, 6H, $C_6H_2CH_3$), 3.14 (t, *J* = 5.8 Hz, NH), 5.60 (s, 4H, $CH(C_6H_5)_2$), 6.70 (s, 4H, C_6H_2), 6.99-7.25 (m, 40H, C_6H_5). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 21.5 ($C_6H_2CH_3$), 29.2 ($C(CH_3)_3$), 30.7 ($CH_2CH_2CH_2$), 38.4 ($C(CH_3)$), 39.6 ($CH_2CH_2CH_2$), 51.1 ($CH(C_6H_5)_2$), 125.8 (C_6H_5), 125.9 (C_6H_5), 128.1 (C_6H_2), 129.3 (C_6H_5), 129.4 ((C_6H_5), 130.2 (C_6H_5), 132.9 (C_6H_5), 143.5 (C_6H_2), 145.3 (C_6H_2), 145.8 (C_6H_2), 158.8 (NCNH). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3455 (vw), 3023 (w), 2955 (w), 2860 (w), 1652 (m), 1492 (m), 1445 (m), 698 (vs), 604 (s). HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{79}H_{80}N_4$ 1084.6379 found 1084.6379.

Synthesis of methyl (2,6-diisopropylphenyl)carbamodithioate:

A solution of NaOH (19.2 g, 480 mmol) in H_2O (24 mL) was mixed with DMSO (200 mL), followed by the addition of 2,6-diisopropylaniline (75.5 mL, 400 mmol) and CS_2 (32.0 mL, 532 mmol). The reaction was stirred at room temperature overnight, resulting in a yellow solution. After cooling the mixture to 0 °C dimethyl sulfate (47.4 mL, 500 mmol) was added dropwise to the solution followed by stirring for 15 minutes at 0 °C. The resulting solution was poured into an ice/water mixture causing a formation of yellow precipitate, which was collected via suction and washed with petroleum ether to isolate methyl (2,6-diisopropylphenyl)carbamodithioate (98.8 g, 392 mmol, 98 %) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.37 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.45 (d, *J* = 6.9 Hz, 6H, $CH(CH_3)_2$), 2.70 (s, 3H, SCH_3), 3.29 (sept, *J* = 6.8 Hz, 2H, $CH(CH_3)_2$), 7.40 (d, *J* = 7.8 Hz, 2H, *m*-C_6H_3), 7.57 (t, *J* = 7.7 Hz, 1H, *p*-C_6H_3), 10.25 (s, 1H, NH). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 19.3 ($C(CH_3)_2$), 23.1 ($C(CH_3)_2$), 24.9 ($C(CH_3)_2$), 28.8 (SCH_3), 124.2 (*m*-C_6H_3), 130.2 (*p*-C_6H_3), 132.6 (*o*-C_6H_3), 147.3 (*i*-C_6H_3), 205.2 (NHCS(SCH_3)).

Synthesis of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea):

1,4-diaminobutane (1.33 mL, 13.3 mmol) was added to a stirred solution of (2,6-diisopropylphenyl)carbamodithioate (7.09 g, 26.5 mmol) in toluene (150 mL) and stirred at 100 °C for two days. Solvent removal followed by washing with pentane gave 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea) (7.96 g, 13.2 mmol, 99 %) as pure white powder.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.15 (d, *J* = 6.9 Hz, 24H, $CH(CH_3)_2$), 1.40 – 1.45 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.07 (sept., *J* = 6.8 Hz,4H, $CH(CH_3)_2$), 3.50 – 3.56 (m, 4H, $CH_2(CH_2)_2CH_2$), 5.38 (t, *J* = 5.8 Hz, 2H, $CSNH(CH_2)_4$), 7.21 (d, *J* = 7.7 Hz, 4H, *m*-C_6H_3), 7.36 (t, *J* = 7.7 Hz, 2H, *p*-C_6H_3), 7.43 (s, 2H, $CSNH(C_6H_3)$). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 23.4 ($CH(CH_3)_2$), 24.6 ($CH(CH_3)_2$), 26.5 ($CH_2(CH_2)_2CH_2$), 28.6 ($CH(CH_3)_2$), 44.5 ($CH_2(CH_2)_2CH_2$), 124.7 (*m*-C_6H_3), 129.8 (*i*-C_6H_3), 130.2 (*p*-C_6H_3), 147.9 (*o*-C_6H_3), 181.7 ($CS(NH)_2$).

Synthesis of (1Z,1'Z)-N,N''-(butane-1,4-diyl)bis(N'-(2,6-diisopropylphenyl)-pyrrolidine-1-carboximidamide) (2c):

Lead(II)oxide (7.42 g, 33.2 mmol) and pyrrolidine (24.8 mL, 302 mmol) were added to a stirred suspension of 1,1'-(butane-1,4-diyl)bis(3-(2,6-diisopropylphenyl)thiourea) (7.96 g, 15.1 mmol) in toluene (150 mL) and the mixture was stirred at 105 °C for three days. After cooling to room temperature the reaction was filtered and the solvent was removed to obtain **2c** as a brownish crude product. Recrystallization from MeCN gave **2c** (7.35 g, 12.2 mmol, 81 %) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.13 (t, *J* = 6.9 Hz, 24H, $CH(CH_3)_2$), 1.25 – 1.31 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.81 – 1.87 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.91 – 2.98 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.02 (sept., *J* = 6.8 Hz,4H, $CH(CH_3)_2$), 3.26 – 3.32 (m, 8H, $NCH_2(CH_2)_2CH_2$), 7.92 (t, *J* = 6.9 Hz, 2H, *p*-C_6H_3), 7.03 (d, *J* = 6.9 Hz, 4H, *m*-C_6H_3). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 23.3 ($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 25.5 ($CH_2(CH_2)_2CH_2$), 28.1 ($CH_2(CH_2)_2CH_2$), 43.8 ($N(CH_2)_2(CH_2)_2$), 48.4 ($N(CH_2)_2(CH_2)_2$), 77.4 ($CH(CH_3)_2$), 121.7 (*m*-C_6H_3), 122.8 (*p*-C_6H_3), 140.3 (*o*-C_6H_3), 145.4 (*i*-

C_6H_3), 151.6 (NC(N(CH_2)$_2$(CH_2)$_2$)$_3$)N). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3403 (w), 2955 (m), 2930 (w), 2862 (w), 1622 (s), 1582 (m), 1522 (m), 1341 (m), 1323 (m), 1278 (m), 780 (m), 751 (s), 702 (m). HR MS (ESI-TOF): [M + H]+ for m/z $C_{38}H_{60}N_6$ 600.4879 found 600.4866.

Synthesis of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea):

1,3-diamino propane (4.45 g, 5.05 mL, 60.0 mmol) was added to a stirred solution of 2,6-dimethylphenyl isothiocyanate (19.6 g, 120 mmol) in toluene (200 mL) followed by stirring at room temperature for 16 hours resulting in a colorless suspension. The precipitate was filtered off and the solvent of the filtrate was removed under reduced pressure giving the raw product, which was further dissolved in DCM (80 mL). After the addition of pentane (200 mL) a white precipitate was formed, which was filtered off, washed with pentane (3x50 mL) and dried in vacuum to obtain 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) (20.3 g, 51.0 mmol, 85%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.62-1.70 (m, 2H, $CH_2(CH_2)CH_2$), 2.23 (s, 12H, $C(CH_3)$), 3.54-3.60 (m, 4H, $CH_2(CH_2)CH_2$), 6.33 (t, *J* = 6.3 Hz, 2H, $NH(CH_2)_3$), 7.09-7.20 (m, 6H, C_6H_3), 7.36 (s, 2H, $NH(C_6H_3)$). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 18.2 ($C(CH_3)$), 30.0 ($CH_2(CH_2)CH_2$), 40.7 ($CH_2(CH_2)CH_2$), 129.2 (*m*-C_6H_3), 129.2 (*p*-C_6H_3), 132.8 (*o*-C_6H_3), 137.6 (*i*-C_6H_3), 181.1 ($SC(NH)_2$).

Synthesis of (1Z,1'Z)-N,N''-(propane-1,3-diyl)bis(N'-(2,6-dimethylphenyl)pyrrolidine-1-carboximidamide) (2e):

Pyrrolidine (5.33 g, 6.15 mL, 75.0 mmol) was added to a stirred suspension of 1,1'-(propane-1,3-diyl)bis(3-(2,6-dimethylphenyl)thiourea) (1.50 g, 3.75 mmol) and lead oxide (1.68 g, 7.50 mmol) in toluene (150 mL) followed by stirring at reflux for 16 hours. After cooling to room temperature the black residue was filtered off and the solvent of the filtrate was removed in vacuum to obtain **2e** (1.70 g, 3.58 mmol, 95%) as a dark yellow waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.62(quint, *J* = 6.5 Hz, 2H, $CH_2(CH_2)CH_2$), 1.68-1.72 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.08 (s, 12H, $C_6H_3CH_3$), 3.00-3.05 (m, 8H, $NCH_2(CH_2)_2CH_2$), 3.16-3.22 (m, 4H, $CH_2CH_2CH_2$), 4.10 (s, 2H, NH), 6.70 (t, *J* = 7.5 Hz, 2H, C_6H_3), 6.90 (d, *J* = 7.4 Hz, 4H, C_6H_3). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 18.8 ($C_6H_3CH_3$), 25.5 ($NCH_2(CH_2)_2CH_2$), 31.3 ($CH_2(CH_2)CH_2$), 40.0 ($CH_2(CH_2)CH_2$), 47.5 ($NCH_2(CH_2)_2CH_2$), 120.4 (*p*-C_6H_3), 127.4 (*m*-C_6H_3), 129.8 (*o*-C_6H_3), 148.2 (*i*-C_6H_3), 150.3 (NHCN). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2930 (w), 2867 (w), 1610 (s), 1580 (s), 1510 (m), 1353 (m), 1332 (m), 981 (m), 829 (m), 756 (s), 702 (m). HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{29}H_{42}N_6$ 474.3471 found 474.3475.

Synthesis of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea):

1,4-diamino butane (1.23 g, 1.40 mL, 14.0 mmol) was added to a stirred solution of phenyl isothiocyanate (3.82 g, 28.3 mmol) in toluene (50 mL) followed by stirring at 50 °C for 68 hours resulting in a colorless suspension. The white precipitate was filtered off, washed with pentane (3x20 mL) and dried in vacuum to obtain 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) (4.45 g, 12.4 mmol, 89%) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6)*: δ (ppm)* = 1.57 (s, 4H, $CH_2(CH_2)_2CH_2$), 3.50 (s, 4H, ($CH_2(CH_2)_2CH_2$), 7.10 (t, *J* = 7.5 Hz, 2H, *p*-C_6H_3), 7.31 (t, *J* = 7.9 Hz, 4H, *m*-C_6H_3), 7.40 (d, *J* = 8.2 Hz, 4H, *o*-C_6H_3), 7.78 (s, 2H, $NH(CH_2)_4$), 9.49 (s, 2H, $NH(C_6H_3)$). ^{13}C{H} NMR (101 MHz, DMSO-d_6): *δ (ppm)* = 26.2 ($CH_2(CH_2)_2CH_2$), 43.7 ($CH_2(CH_2)_2CH_2$), 123.1 (*o*-C_6H_3), 124.1 (*m*-C_6H_3), 128.7 (*p*-C_6H_3), 139.2 (*i*-C_6H_3), 180.3 ($SC(NH)_2$).

Synthesis of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine):

Triethyl amine (7.10 g, 9.73 mL, 70.2 mmol) was added to a stirred suspension of 1,1'-(butane-1,4-diyl)bis(3-phenylthiourea) (12.6 g, 35.1 mmol) in DCM (150 mL) followed by addition of triphenyl phosphane (20.3 g, 77.2 mmol) and carbon tetrachloride (10.8 g, 6.76 mL, 70.2 mmol). After stirring at reflux for 16 hours, the solvent was removed under

vacuum and the resulting waxy solid was extracted with pentane (50 mL) and hexanes (here a mixture of hexanes was used) (2x50 mL). After solvent removal an mixture of a white solid and a clear oil was obtained, which was further extracted with pentane (20 mL). Solvent removal gave N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) (1.54 g, 5.30 mmol, 15 %) as a clear oil.

^{1}H NMR (400 MHz, C_6D_6)*: δ (ppm)* = 1.25-1.29 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.82-2.86 (m, $CH_2(CH_2)_2CH_2$), 6.87-6.91 (m, 2H, *p*-C_6H_5), 7.04-7.08 (m, 4H, *m*-C_6H_5), 7.12-7.15 (m, *o*-C_6H_5). ^{13}C{H} NMR (101 MHz, C_6D_6): *δ (ppm)* = 28.6 ($CH_2(CH_2)_2CH_2$), 46.1 ($CH_2(CH_2)_2CH_2$), 124.0 (*m*-C_6H_5), 124.0 (*p*-C_6H_5), 129.8 (*o*-C_6H_5), 136.2 (*i*-C_6H_5), 141.3 (NCN).

Synthesis of (1Z,1'Z)-N',N'''-(butane-1,4-diyl)bis(N-phenylpyrrolidine-1-carboximidamide) (2f):

Pyrrolidine (6.86 g, 7.92 mL, 96.4 mmol) was added to a stirred solution of N,N'-(butane-1,4-diyl)bis(N-phenylmethanediimine) (1.40 g, 4.82 mmol) in MeCN (100 mL) followed by stirring at reflux for 16 hours. After solvent removal the resulting brown oil was suspended in water (50 mL) and HCl was added until pH 2 was reached. After stirring for several minutes toluene (50 mL) and a solution of NaOH were added until pH 12 was reached. The organic phase was separated, dried over $MgSO_4$ and the solvent was removed to obtain **2f** (1.24 g, 2.87 mmol, 59 %) as a brown waxy solid.

^{1}H NMR (300 MHz, $CDCl_3$)*: δ (ppm)* = 1.33-1.39 (m, 4H, $CH_2(CH_2)_2CH_2$), 1.79-1.84 (m, 8H, $NCH_2(CH_2)_2CH_2$), 2.96-3.01 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.23-3.27 (m, 8H, $NCH_2(CH_2)_2CH_2$), 6.76-6.84 (m, 5H, C_6H_5), 7.14-7.19 (m, 5H, C_6H_5). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 25.5 ($NCH_2(CH_2)_2CH_2$), 27.6 ($CH_2(CH_2)_2CH_2$), 43.8 ($CH_2(CH_2)_2CH_2$), 48.1 ($NCH_2(CH_2)_2CH_2$), 120.2 (*p*-C_6H_5), 122.6 (*m*-C_6H_5), 128.9 (*o*-C_6H_5), 151.3 (*i*-C_6H_5), 153.3 (NHCN). IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2962 (w), 2928 (w), 2872 (w), 1576 (s), 1512 (s), 1485 (s), 1394 (s), 1347 (s), 1143 (m), 780 (m), 695 (s), 501 (s). HRMS (ESI-TOF): $[M + H]^+$ for m/z $C_{26}H_{36}N_6$ 432.3001 found 432.3005.

Complex synthesis

Synthesis of 3a:

CH_3MgI (0.39 mL, 1.10 mmol, 3.0 M in Et_2O) was added to a stirred solution of **1a** (300 mg, 0.55 mmol) in toluene (3 mL) followed by stirring at room temperature overnight yielding a white slurry. The solids were filtered off and a few drops THF were added to the filtrate causing the instant formation of clear crystals. Filtration and washing of crystals with *n*-pentane gave **3a** (450 mg, 0.39 mmol, 72%) as clear, colourless crystals.

^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 1.28 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.37 (m, 12H, CH(C*H*$_3$)$_2$) 1.43 (s, 18H, C(C*H*$_3$)$_3$), 3,58-3.65 (m, 4H, C*H*(CH$_3$)$_2$), 4.11 (s, 4H, C*H*$_2$C*H*$_2$) 6.94-7.08 (m, 6H, C_6H_3). ^{1}H NMR (400 MHz, THF-d_8): *δ(ppm)* = 1.16 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.23 (s, 18H, C(C*H*$_3$)$_3$) 1.25 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3,45 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 3.79 (s, 4H, C*H*$_2$C*H*$_2$) 6.79-6.83 (m, 2H, C_6H_3), 6.90-6.93 (m, 4H, C_6H_3); ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): *δ (ppm)* = 24.1 (CH(CH$_3$)$_2$), 25.5 (CH(CH$_3$)$_2$), 28.6 (CH(CH$_3$)$_2$), 31.0 (C(CH$_3$)$_3$), 41.5 (C(CH$_3$)$_3$, 52.6Dipp (CH$_2$CH$_2$), 122.5 (*p*-C$_6$H$_3$), 123.6 (*m*-C$_6$H$_3$), 143.0 (*o*-C$_6$H$_3$), 148.8 (*i*-C$_6$H$_3$), 178.0 (NCN). Notably, the resonance at 25.5 ppm overlaps with the solvent peak, but its presence was verified by ^{13}C-DEPT NMR spectroscopy; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2959 (m), 2868 (w), 1652 (w), 1625 (w), 1458 (s), 1402 (s), 1286 (m), 1170 (m), 1023 (s), 876 (s), 762 (s); Anal. calc. (found) for [$C_{52}H_{88}I_2Mg_2N_4O_4$ 0.15 toluene]: C 55.43 (55.56), H 7.82 (7.56), N 4.87 (4.74).

Synthesis of 4a:

CH_3MgI (0.96 mL, 2.88 mmol, 3.0 M in Et_2O) was added to a stirred solution of **1a** (750 mg, 1.37 mmol) in toluene (10 mL) followed by stirring at room temperature overnight yielding a white slurry. The solution was filtered directly into a flask loaded with a freshly prepared potassium mirror (715 mg, 18.3 mmol) and toluene (30 mL)

was added to reach all spots of the potassium mirror. After stirring for two days at room temperature, the black suspension was filtered and the filtrate was concentrated in vacuum to obtain a yellowish solid. Recrystallization from Et_2O gave **4a** (577 mg, 0.51 mmol, 37%) as clear, colourless crystals.

^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 0.43 (d, *J* = 4.5 Hz, 6H, CH(C*H*$_3$)$_2$), 1.24-1.26 (m, 24H, CH(C*H*$_3$)$_2$ & C(C*H*$_3$)$_3$), 1.35 (d, *J* = 4.6 Hz, 12H, CH(C*H*$_3$)$_2$), 3.16 (sept, *J* = 4.6 Hz, 2H, C*H*(CH$_3$)$_2$), 3.50-3.54 (m, 4H, C*H*(CH$_3$)$_2$ & C*H*$_2$C*H*$_2$), 4.45-4.50 (m, 2H, C*H*$_2$C*H*$_2$), 6.94-6.95 (m, 2H, C$_6$*H*$_3$), 7.01-7.07 (m, 4H, C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): *δ (ppm)* = 22.5 (CH(CH$_3$)$_2$), 22.8 (CH(CH$_3$)$_2$), 23.6 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 28.2 (CH(CH$_3$)$_2$), 28.8 (CH(CH$_3$)$_2$), 29.7 (C(CH$_3$)$_3$), 41.4 (C(CH$_3$)$_3$), 54.9 (CH$_2$CH$_2$), 122.9 (*p*-C$_6$H$_3$), 123.2 (*m*-C$_6$H$_3$), 123.3 (*m*-C$_6$H$_3$), 140.9 (*o*-C$_6$H$_3$), 142.1 (*o*-C$_6$H$_3$), 145.5 (*i*-C$_6$H$_3$), 179.8 (NCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960 (m), 2868 (w), 1623 (m), 1585 (m), 1512 (m), 1429 (m), 1216 (m), 765 (m); Anal. calc. (found) for [$C_{72}H_{112}Mg_2N_8$ 0.95 toluene]: C 77.06 (76.73), H 9.83 (9.48), N 9.14 (9.28).

Synthesis of 4b:

CH_3MgI (2.10 mL, 6.18 mmol, 3.0 M in Et_2O) was added to a stirred solution of **1b** (1.65 g, 2.94 mmol) in toluene (10 mL) followed by stirring at room temperature overnight yielding a yellow to brown solution and a white precipitate. The solids were filtered off and the filtrate was concentrated to one third, causing the formation of crystals at room temperature overnight. The crystals were collected and washed with *n*-pentane (2x5 mL) to obtain **4b** (2.85 g, 2.44 mmol, 83%) as clear colourless blocks.

^{1}H NMR (400 MHz, THF-*d*$_8$): *δ(ppm)* = 1.07-1.21 (m, 84H, CH(C*H*$_3$)$_2$ & C(C*H*$_3$)$_3$), 1.92-2.09 (br s, 4H, CH$_2$C*H*$_2$CH$_2$), 3.13-3.31 (br s, 8H, C*H*(CH$_3$)$_2$), 3.62-3.74 (br s, 8H, C*H*$_2$CH$_2$C*H*$_2$), 6.72-6.80 (m, 12H, C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, THF-*d*$_8$): *δ (ppm)* = 23.8 (CH(CH$_3$)$_2$), 24.6 (C(CH$_3$)$_3$), 28.5 (CH(CH$_3$)$_2$), 31.3 (C(CH$_3$)$_3$), 41.2 (CH$_2$(CH$_2$)CH$_2$), 48.0 (CH$_2$(CH$_2$)CH$_2$), 122.0 (*p*-C$_6$H$_3$), 123.2 (*m*-C$_6$H$_3$), 142.3 (*o*-C$_6$H$_3$), 149.1 (*i*-C$_6$H$_3$), 178.0

(NCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2955 (m), 2923 (w), 2866 (w), 1651 (w), 1411 (vs), 1340 (s), 1322 (s), 1171 (m), 765 (s), 728 (m); Anal. calc. (found) for [$C_{74}H_{116}Mg_2N_8$ 1.40 toluene]: C 77.70 (77.31), H 9.90 (9.47), N 8.69 (8.65).

Synthesis of 5a:

Mg(*n*-Bu)$_2$ (1.50 mL, 1.50 mmol, 1.0 M in heptane) was added to a stirred solution of **2a** (400 mg, 0.70 mmol) in toluene (4 mL) followed by stirring at 105 °C overnight. After solvent concentration to one third and standing at room temperature for two weeks **5a** (262 mg, 0.44 mmol, 63%) was obtained as colourless crystals.

^{1}H NMR (400 MHz, C_6D_6/THF-d_8): *δ(ppm)* = 1.20 (dd, *J* = 9.0 Hz, 24H, CH(CH_3)$_2$), 1.37-1.40 (m, 8H, NCH$_2$(CH_2)$_2$CH$_2$), 2.97-3.00 (m, 8H, NCH_2(CH$_2$)$_2$CH_2), 3.14-3.16 (m, 4H, CH_2CH_2), 3,21 (sept, *J* = 7.0 Hz, 4H, CH(CH$_3$)$_2$), 6.89-6.93 (m, 2H, *p*-C$_6H_3$), 7.03-7.05 (m, 4H, *m*-C$_6H_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6/THF-d_8): *δ (ppm)* = 23.3 (CH(CH$_3$)$_2$), 23.7 (CH(CH$_3$)$_2$), 25.6 (CH$_2$CH$_2$), 28.6 (CH(CH$_3$)$_2$), 44.5 (NCH$_2$(CH$_2$)$_2$CH$_2$), 48.1 (NCH$_2$(CH$_2$)$_2$CH$_2$), 121.5 (*p*-C$_6$H$_3$), 122.8 (*m*-C$_6$H$_3$), 139.8 (*o*-C$_6$H$_3$), 146.7 (*i*-C$_6$H$_3$), 149.8 (NCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2955 (m), 2863 (w), 1615 (m), 1582 (m), 1354 (m), 749 (m); despite repeated attempts no suitable elemental analysis could be obtained.

Synthesis of 5e:

Mg(HMDS)$_2$ (79.0 mg, 0.46 mmol) was added to a stirred solution of **2e** (100 mg, 0.21 mmol) in toluene (5 mL) and stirred at room temperature overnight. Solvent removal and recrystallization from *n*-hexane/Et$_2$O (7:1) at room temperature gave **5e** (64 mg, 0.13 mmol, 61%) as clear colourless crystals.

^{1}H NMR (400 MHz, toluene-d_8): *δ(ppm)* = 1.13-1.21 (m, 4H, CH$_2$(CH_2)CH$_2$), 1.34-1.47 (m, 8H, N(CH$_2$(CH_2)$_2$CH$_2$), 2.04 (s, 3H, C$_6$H$_3$(CH_3)$_2$), 2.20 (s, 3H, C$_6$H$_3$(CH_3)$_2$), 2.56 (s, 3H, C$_6$H$_3$(CH_3)$_2$), 2.64 (s, 3H, C$_6$H$_3$(CH_3)$_2$), 3.09-3.25 (m, 8H, N(CH_2(CH$_2$)$_2$CH_2), 3.35-3.55 (m,

2H, C*H*$_2$(CH$_2$)C*H*$_2$), 6.65-7.08 (m, 6H, C$_6$*H*$_3$); Due to the low solubility of **5e** no proper ^{13}C NMR spectrum could be obtained; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2967 (w), 2847 (w), 2912 (w), 2878 (w), 1505 (vs), 1487 (s), 1392 (vs), 1363 (m), 1331 (m), 857 (w), 755 (s), 729 (s); Anal. calc. (found) for [$C_{29}H_{40}MgN_6$ 0.4 toluene]: C 71.55 (71.15), H 8.16 (8.10), N 15.74 (15.42).

Synthesis of 5f:

CH_3MgI (0.54 mL, 1.62 mmol, 3.0 M in Et_2O) was added to a stirred solution of **2f** (350 mg, 0.81 mmol) in THF (10 mL) followed by stirring at room temperature overnight. The white precipitate formed was filtered off and the solvent of the filtrate was removed. The crude product was recrystallized from a mixture of toluene/THF (7:1) layered with *n*-pentane at -20°C. **5f** (282 mg, 0.62 mmol, 76%) was obtained as clear colourless blocks.

^{1}H NMR (400 MHz, THF-d_8): *δ(ppm)* = 1.59 (br, 4H, CH$_2$(C*H*$_2$)$_2$CH$_2$), 1.72-1.75 (m, 8H, N(CH$_2$(C*H*$_2$)$_2$CH$_2$), 3.08 (br, 4H, C*H*$_2$(CH$_2$)$_2$C*H*$_2$), 3.23-3.26 (m, 8H, N(C*H*$_2$(CH$_2$)$_2$C*H*$_2$), 6.45-6.49 (m, 2H, *p*-C$_6$*H*$_5$), 6.64-6.66 (m, 4H, *m*-C$_6$*H*$_5$), 6.93-6.97 (m, 4H, *o*-C$_6$*H*$_5$); ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): *δ (ppm)* = 26.2 (NCH$_2$(CH$_2$)$_2$CH$_2$), 30.8 (CH$_2$(CH$_2$)$_2$CH$_2$), 48.9 (CH$_2$(CH$_2$)$_2$CH$_2$), 49.5 (NCH$_2$(CH$_2$)$_2$CH$_2$), 117.4 (*p*-C$_6$H$_5$), 121.5 (*m*-C$_6$H$_5$), 129.1 (*o*-C$_6$H$_5$), 154.6 (*i*-C$_6$H$_5$), 166.4 (NHCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3055 (vw), 2970 (vw), 2920 (vw), 1594 (w), 1506 (m), 1473 (m), 1400 (s), 1334 (m), 1275 (m), 993 (m), 736 (vs), 697 (vs); Anal. calc. (found) for [$C_{26}H_{34}MgN_6$ 0.10 toluene]: C 69.10 (69.09), H 7.56 (7.46), N 18.11 (18.02).

Synthesis of 6b:

Mg(*n*-Bu)$_2$ (0.35 mL, 0.35 mmol, 1.0 M in heptane) was added to a stirred solution of **2b** (200 mg, 0.35 mmol) in toluene (5 mL) followed by stirring at room temperature

overnight. Solvent removal gave a yellow solid which was further washed with *n*-pentane to obtain **6b** (142 mg, 0.23 mmol, 67%) as a white crystalline solid. Crystals suitable for X-Ray diffraction analysis grew from the *n*-pentane washing solution.
^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 0.54 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.16 (d, *J* = 6.8 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24-1.29 (m, 16H, N(CH$_2$(C*H*$_2$)$_2$CH$_2$)), 1.38 (d, *J* = 7.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.53 (d, *J* = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 2.34-2.41 (m, 4H, CH$_2$(C*H*$_2$)CH$_2$), 2.96-3.00 (m, 8H, N(C*H*$_2$(CH$_2$)$_2$C*H*$_2$)), 3.06-3.13 (m, 12H, C*H*(CH$_3$)$_2$ & N(C*H*$_2$(CH$_2$)C*H*$_2$)), 3.45-3.52 (m, 4H, C*H*$_2$(CH$_2$)C*H*$_2$), 3.61-3.67 (m, 4H, C*H*$_2$(CH$_2$)C*H*$_2$), 3.89-3.96 (m, 4H, C*H*(CH$_3$)$_2$), 7.00-7.07 (m, 8H, *m*-C$_6$*H*$_3$), 7.14-7.21 (m, 4H, *p*-C$_6$*H*$_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): *δ (ppm)* = 23.0 (CH(CH$_3$)$_2$), 23.3 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 25.1 (CH(CH$_3$)$_2$), 25.8 (NCH$_2$(CH$_2$)$_2$CH$_2$), 27.5 (CH(CH$_3$)$_2$), 28.8 (CH(CH$_3$)$_2$), 40.8 (CH$_2$(CH$_2$)CH$_2$), 46.5 (CH$_2$(CH$_2$)CH$_2$), 48.5 (NCH$_2$(CH$_2$)$_2$CH$_2$), 122.2 (*p*-C$_6$H$_3$), 122.6 & 122.9 (*m*-C$_6$H$_3$), 142.0 & 143.4 (*o*-C$_6$H$_3$), 145.3 (*i*-C$_6$H$_3$), 166.0 (NCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2960 (w), 2866 (vw), 1417 (vs), 1357 (m), 1336 (s), 772 (m), 731 (s); Anal. calc. (found) for [$C_{74}H_{112}N_{12}Mg_2$]: C 72.95 (72.86), H 9.27 (9.13), N 13.80 (13.39).

Synthesis of 7:

Mg(*n*-Bu)$_2$ (0.31 mL, 0.31 mmol, 1.0 M in heptane) was added to a stirred solution of **2d** (200 mg, 0.31 mmol) in toluene (5 mL) followed by stirring at room temperature overnight. Solvent removal gave a yellow solid, which was redissolved in pentane. After some minutes **7** (103 mg, 0.15 mmol, 50%) precipitated as a colourless solid. Despite repeated attempts using various solvents and solvent combinations we could not obtain single crystals.
^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = 1.07-1.13 (m, 20H, CH(C*H*$_3$)$_2$ & N(CH$_2$(C*H*$_2$)$_2$CH$_2$)), 1.28 (d, *J* = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 2.97-3.00 (m, 8H, N(*C*H$_2$(CH$_2$)$_2$*C*H$_2$), 3.50-3.64 (m, 4H, C*H*(CH$_3$)$_2$), 4.36 (s, 4H, C*H*$_2$(C$_6$H$_4$)), 7.03-7.10 (m, 6H, C$_6$*H*$_3$), 7.30-7.56 (m, 4H, C$_6$*H*$_4$); ^{1}H NMR (400 MHz, toluene-*d*$_8$): *δ(ppm)* = 1.00 (br, 12H, CH(C*H*$_3$)$_2$), 1.16-1.20 (m, 8H,

N($CH_2(CH_2)_2CH_2$), 1.25 (d, *J* = 6.8 Hz, 12H, CH($CH_3)_2$), 2.96-3.00 (m, 8H, N($CH_2(CH_2)_2CH_2$), 3.51 (br, 4H, $CH(CH_3)_2$, 4.30 (s, 4H, $CH_2(C_6H_4)$), 6.98-7.45 (m, 10H, C_6H_3+C_6H_4); ^{1}H NMR (400 MHz, THF-d_8): signals have not been assigned due to complexity, for details see Figures S6-8; $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): *δ (ppm)* = 23.1 ($CH(CH_3)_2$), 24.7 ($CH(CH_3)_2$), 25.6 ($NCH_2(CH_2)_2CH_2$), 28.1 ($CH(CH_3)_2$), 48.5 ($NCH_2(CH_2)_2CH_2$), 52.1 ($CH_2C_6H_4$), 123.0 (*p*-C_6H_3), 123.1 (*m*-C_6H_3), 124.9 (*o*-C_6H_4), 125.8 (*o*-C_6H_4), 128.7 (*m*-C_6H_4), 142.9 (*o*-C_6H_3), 144.8 (*i*-C_6H_4), 144.9 (*i*-C_6H_3), 166.8 (NCN); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2958 (w), 2866 (vw), 1452 (vs), 1325 (m), 1282 (m), 776 (m), 728 (m); Anal. calc. (found) for [$C_{42}H_{58}N_6Mg$]: C 75.15 (75.03), H 8.71 (8.87), N 12.52 (12.27).

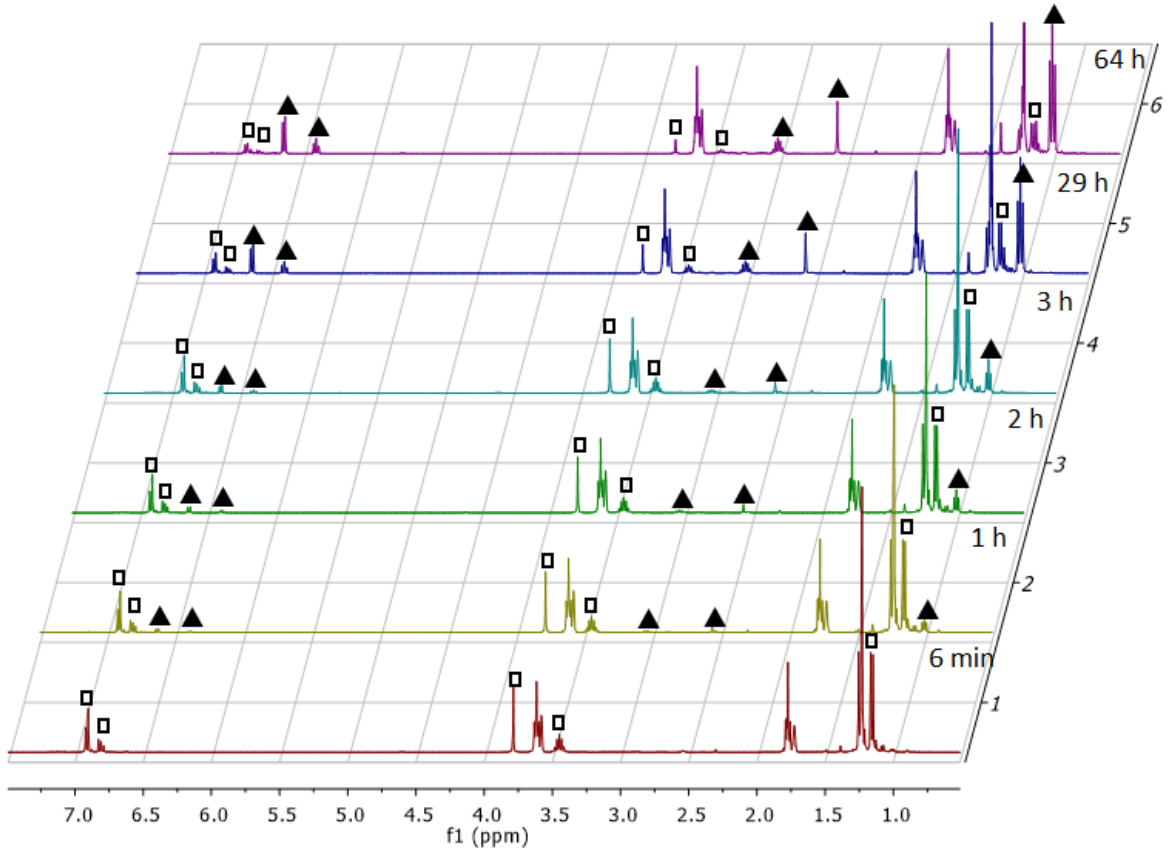

Figure S1 ^{1}H NMR spectrum (400 MHz) of the time-dependent conversion of 3a to 4a in THF-d_8 at 300K. ◘= 3a; ▲= 4a.

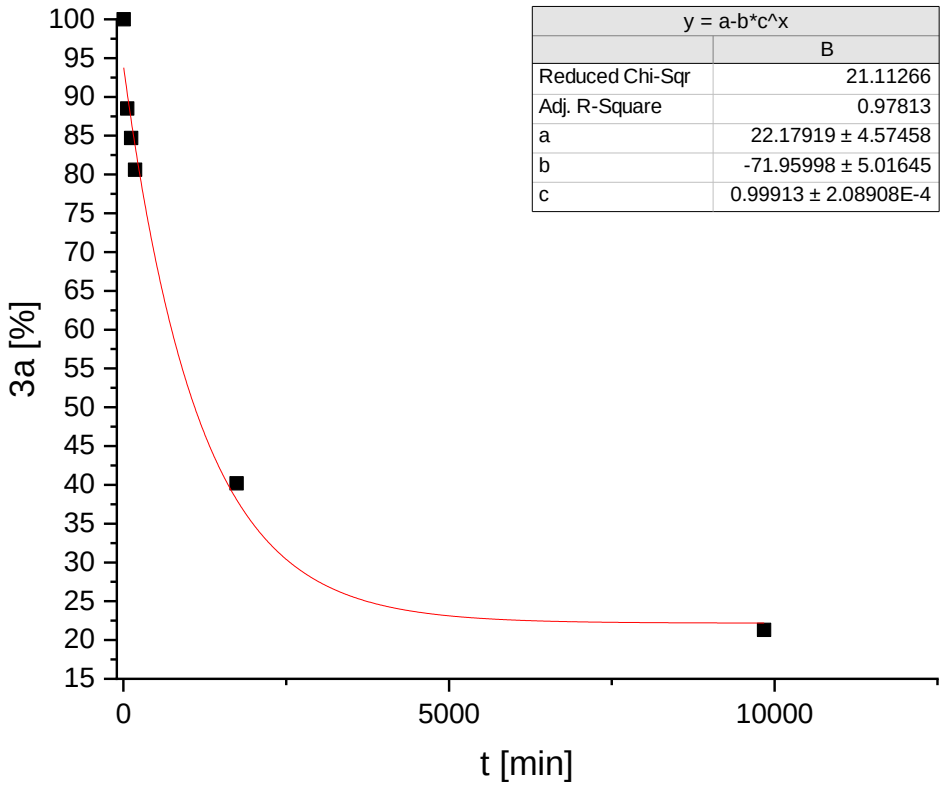

Figure S2 Abundance of 3a in THF-d_8 solution over time.

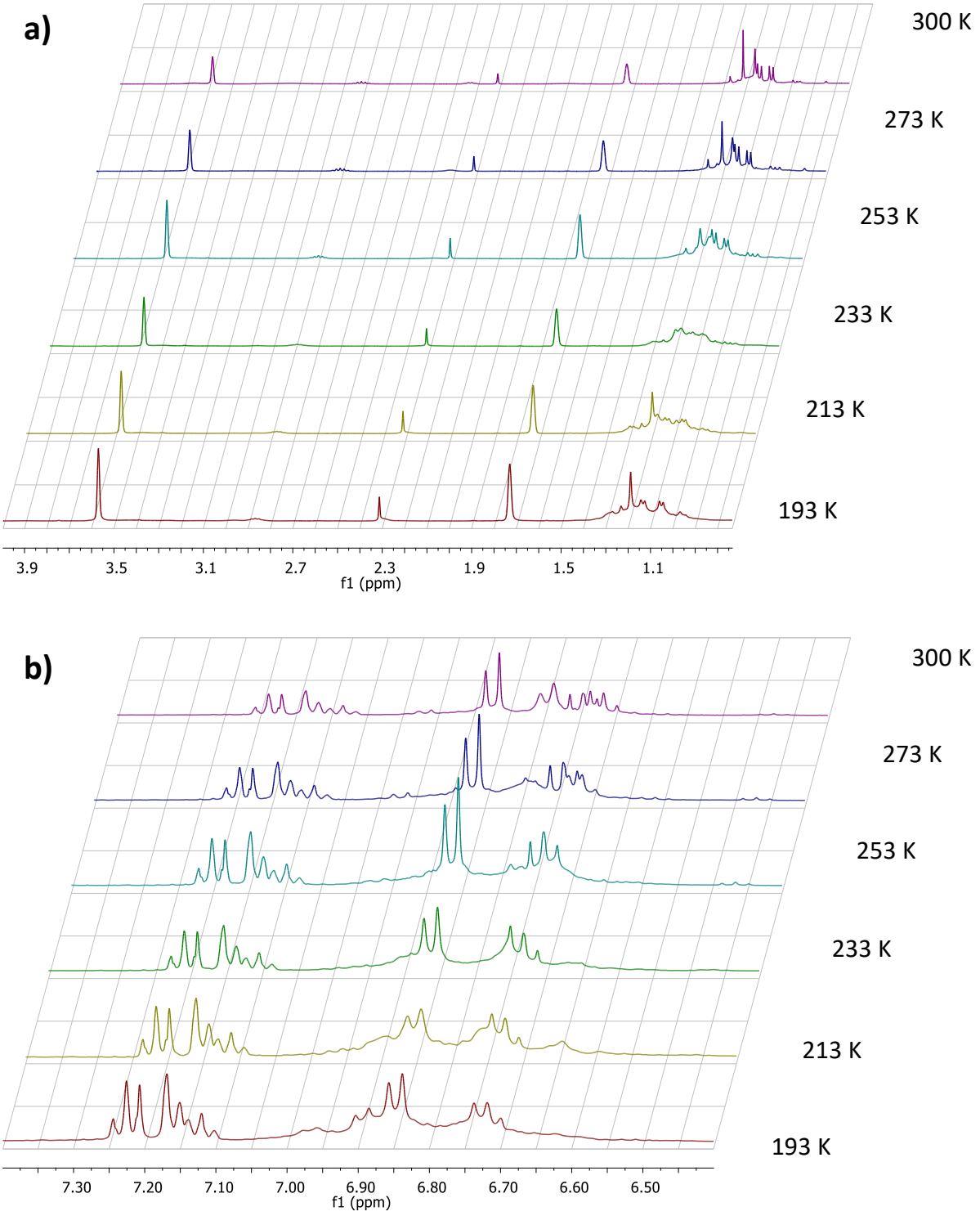

Figure S3 Excerpts (a) 0.9 – 4.0 ppm and b) 6.4 – 7.5 ppm) of the ^{1}H NMR spectra of a solution of 4b in THF-d_8 at different temperatures**.**

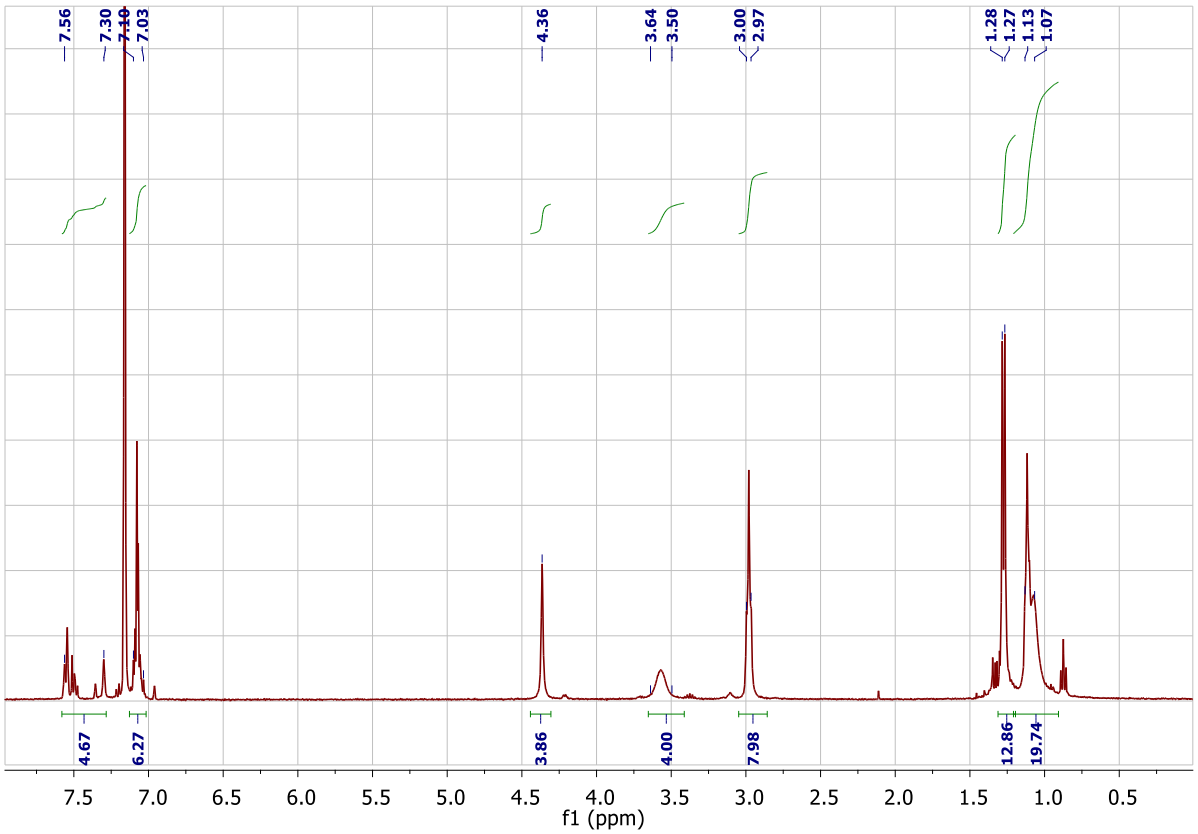

Figure S4 ^{1}H NMR spectrum (400 MHz) of 7 in C_6D_6 at 300 K.

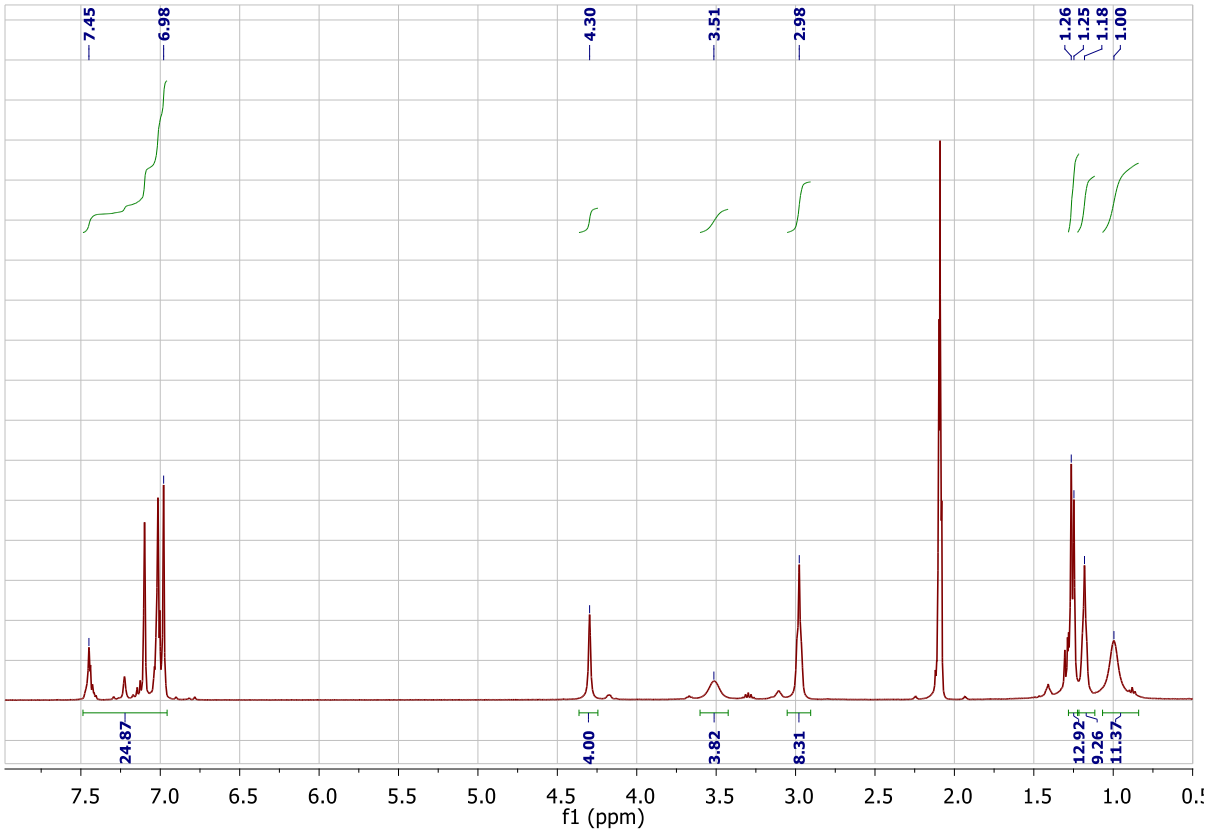

Figure S5 ^{1}H NMR spectrum (400 MHz) of 7 in toluene-d_8 at 300 K.

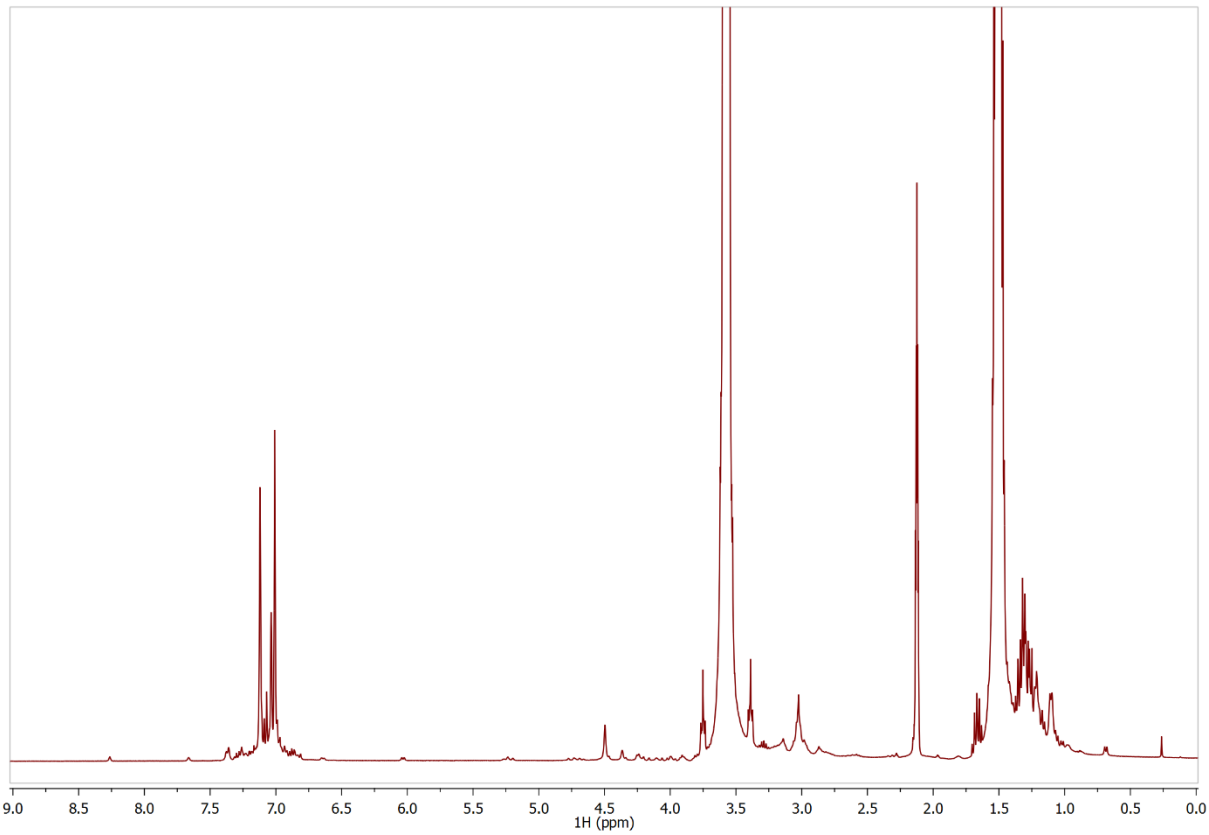

Figure S6 ^{1}H NMR spectrum (400 MHz) of 7 in toluene-d_8 and about 20 eq. of THF at 297 K.

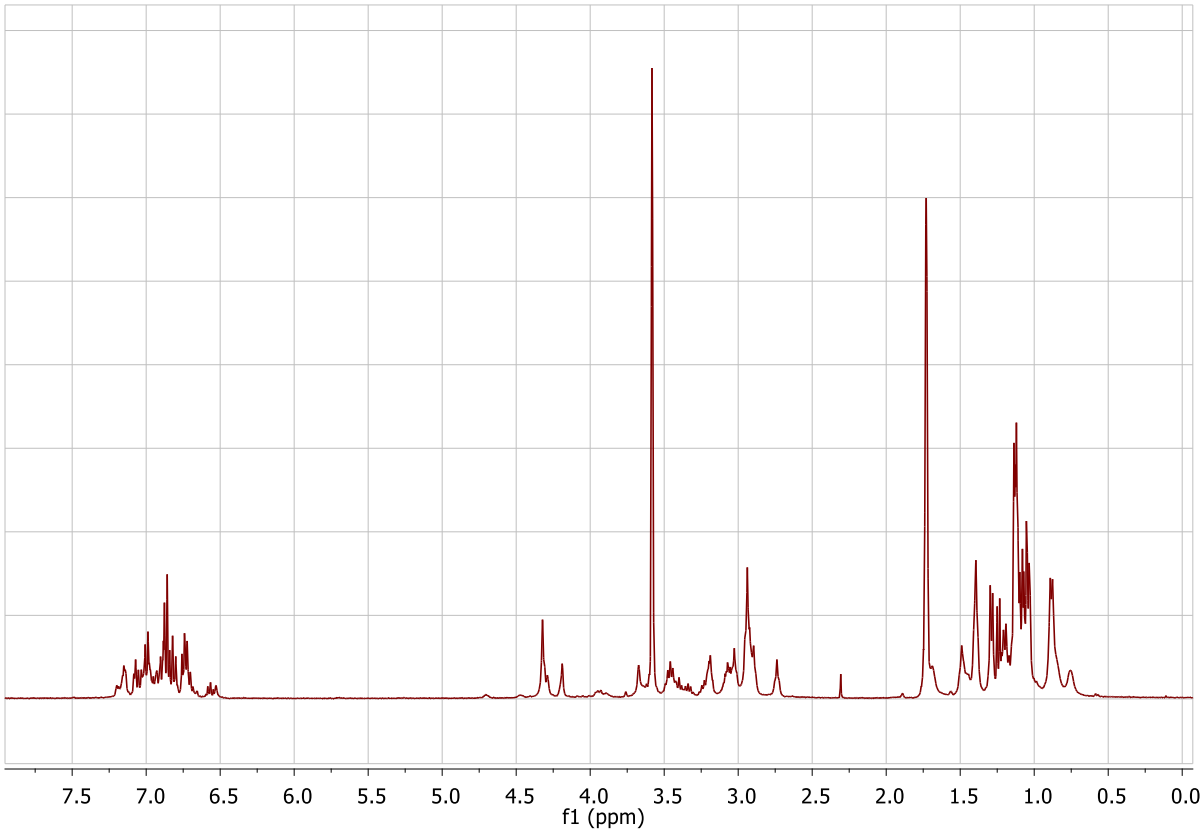

Figure S7 ^{1}H NMR spectrum (400 MHz) of 7 in THF-d_8 at 300 K.

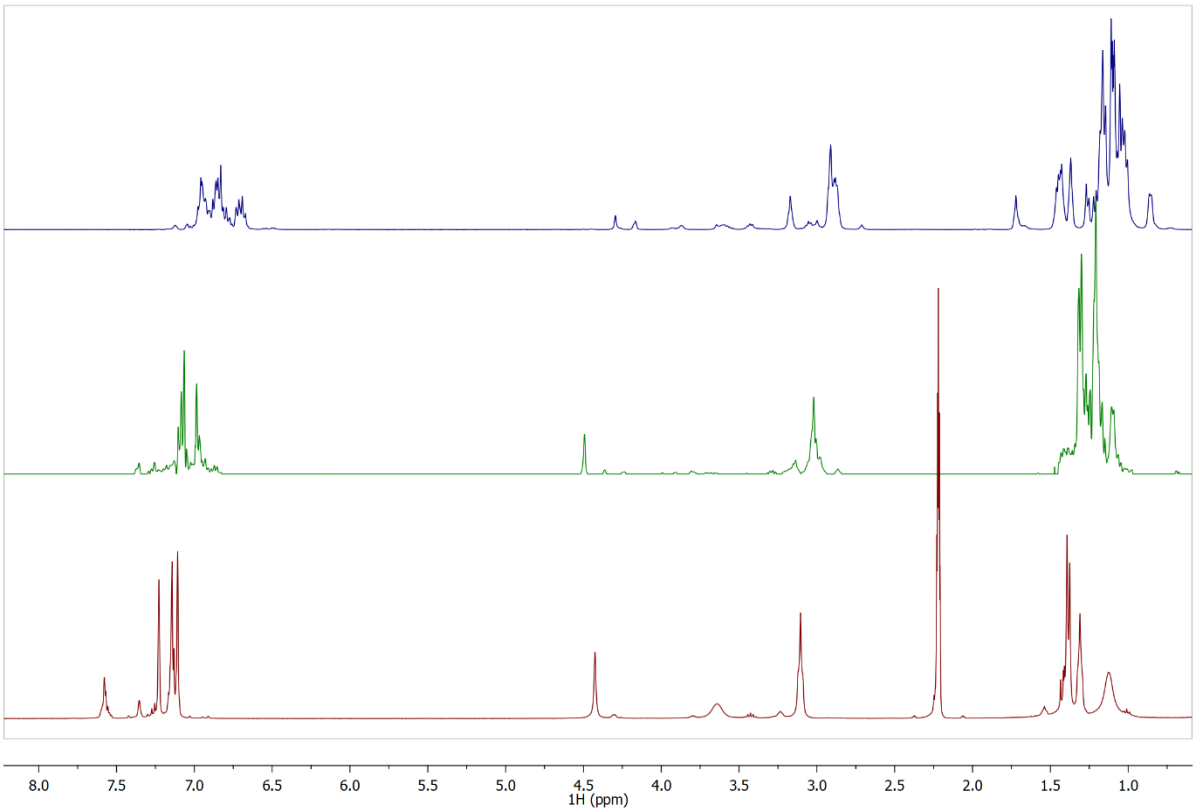

Figure S8 ^{1}H NMR spectra (400 MHz, 297 K) of 7 in toluene-d_8 (red) and in toluene-d_8 along with about 20 eq. of THF (green) along with a diffusion filtered ^{1}H NMR spectrum (400 MHz, 297 K) of 7 in THF-d_8 (blue).

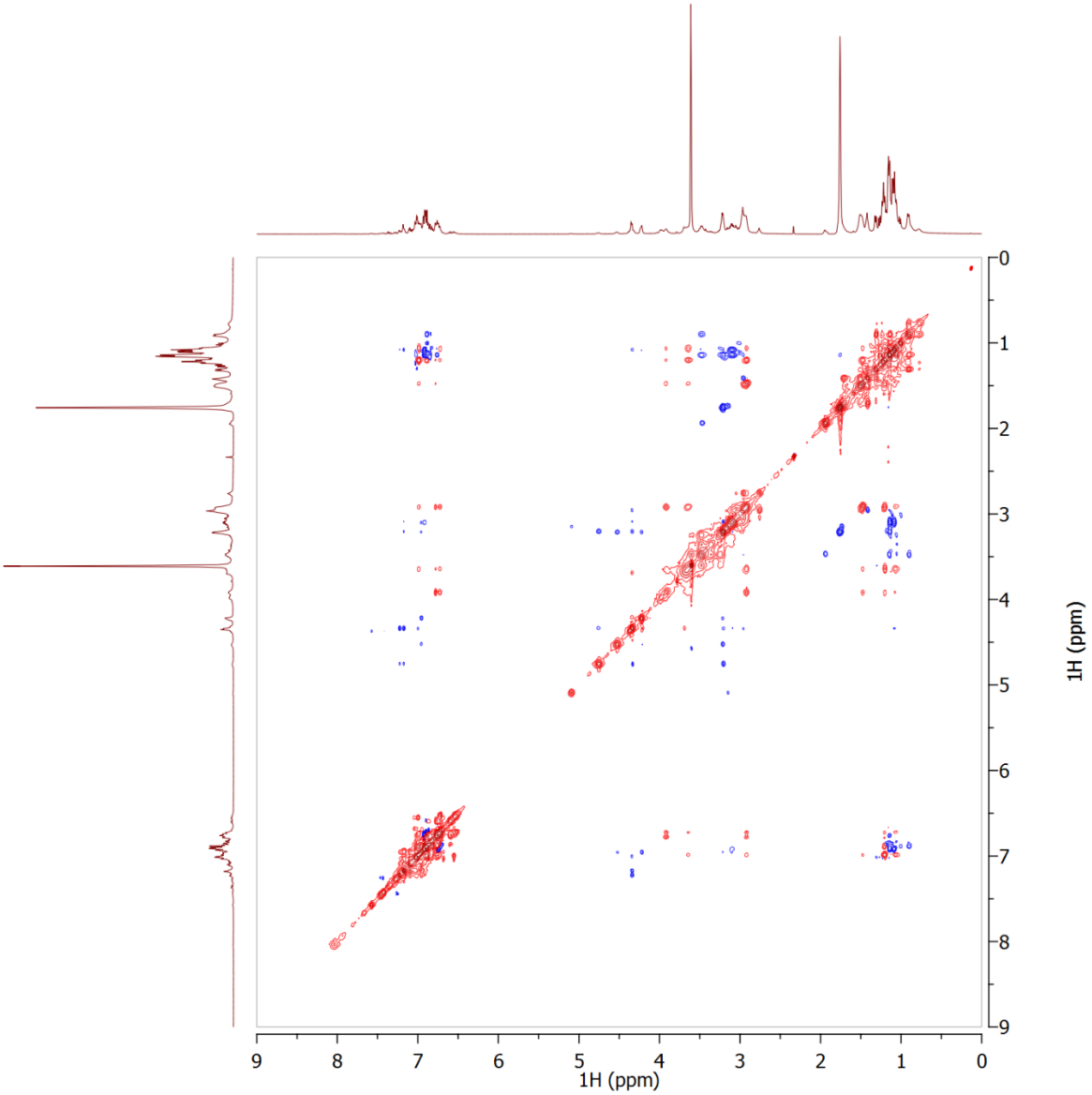

Figure S9 EXSY NMR spectrum (400 MHz) of 7 in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

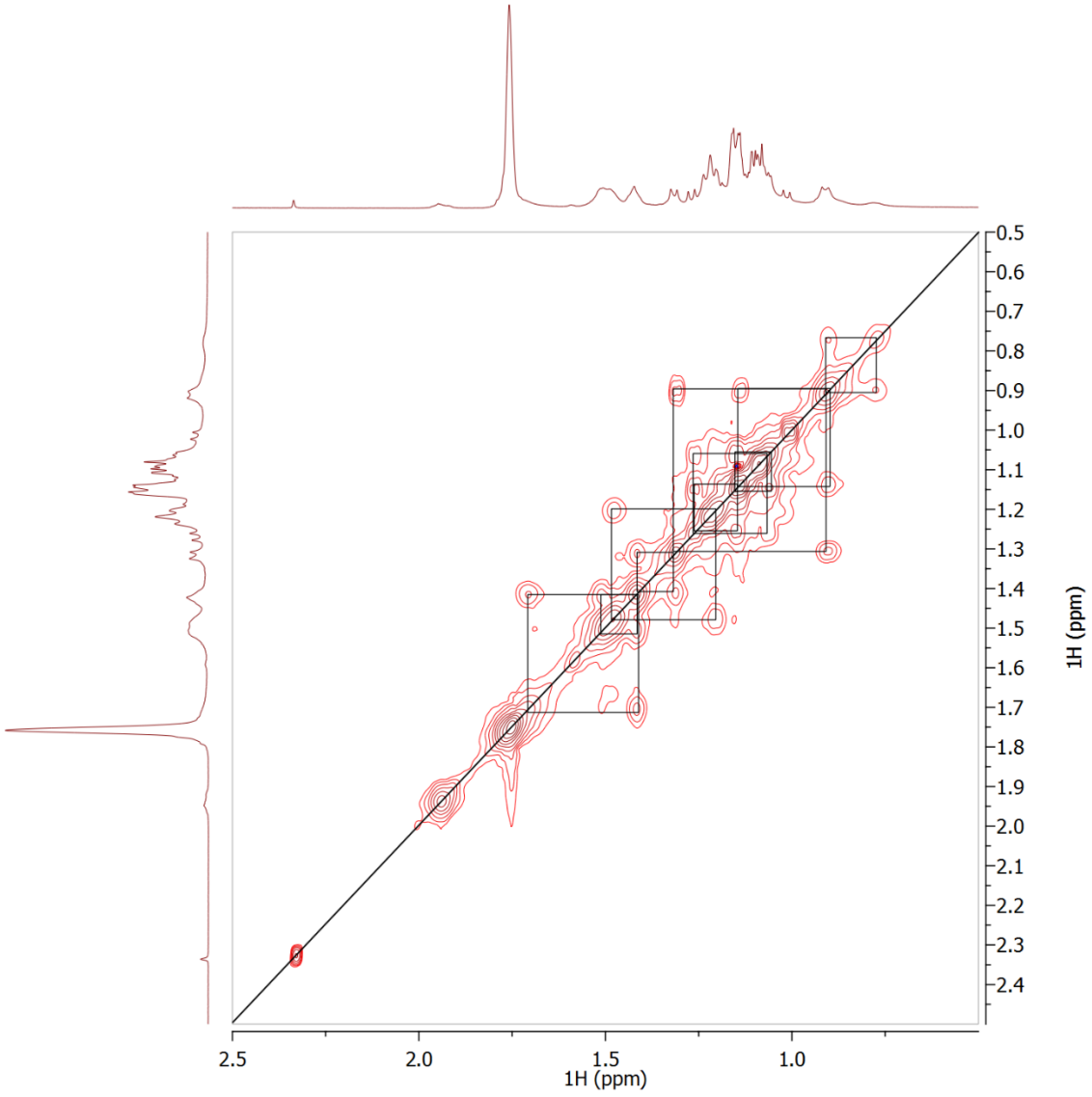

Figure S10 Excerpt (methyl and methylene resonances) of the EXSY NMR spectrum (400 MHz) of 7 in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

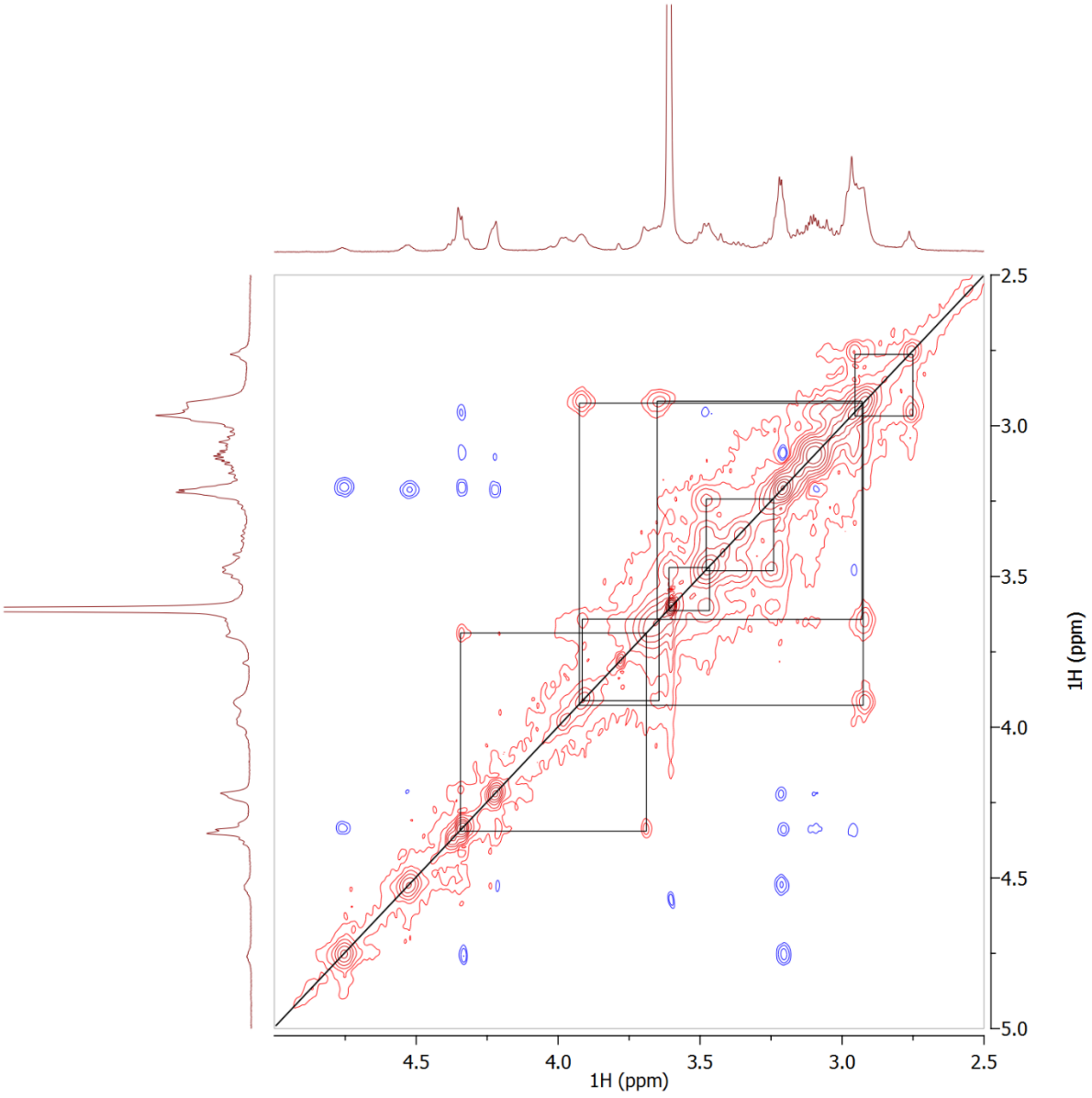

Figure S11 Excerpt (methylene and methine resonances) of the EXSY NMR spectrum (400 MHz) of 7 in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

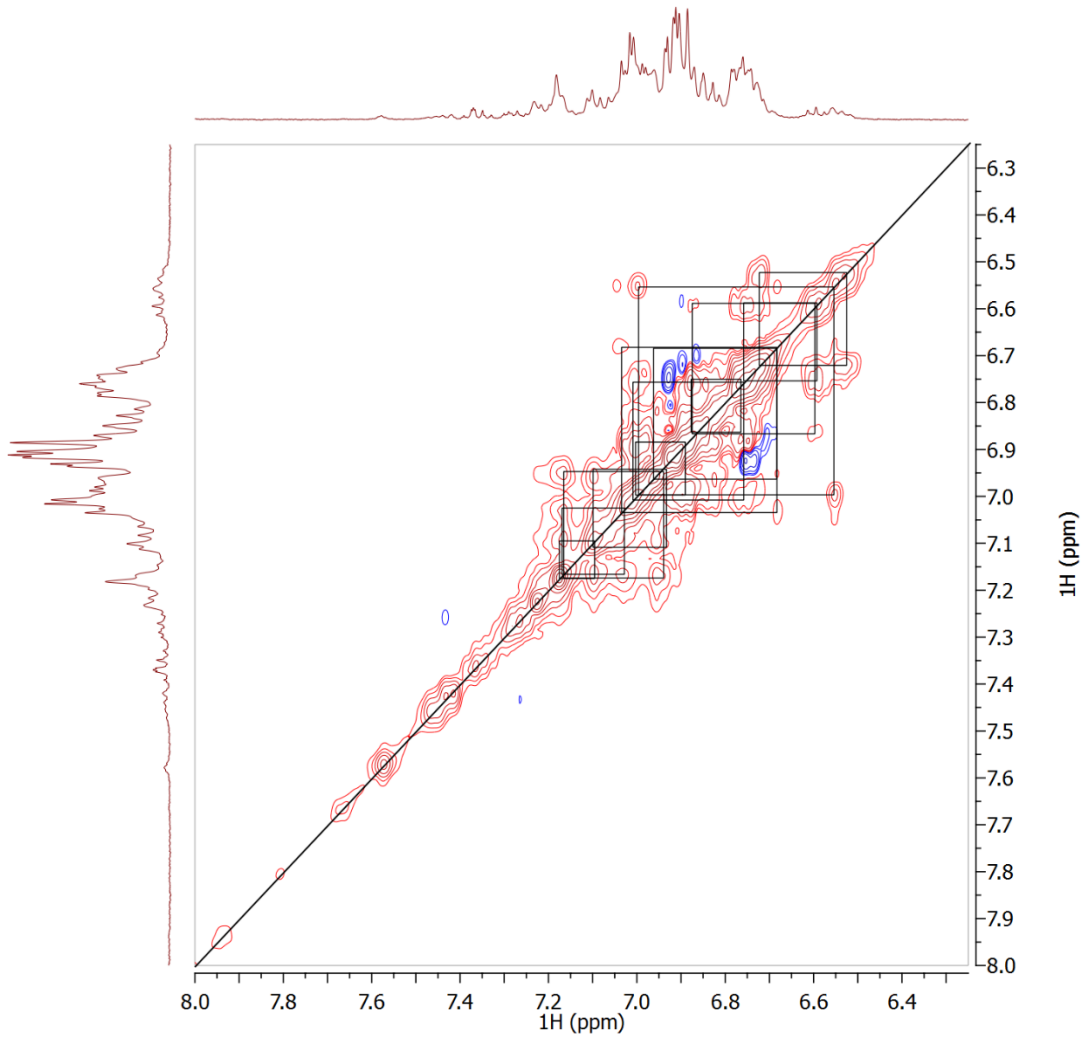

Figure S12 Excerpt (aromatic CH resonances) of the EXSY NMR spectrum (400 MHz) of 7 in THF-d_8 at 297 K using a mixing time of t_m = 1.0 s, a resolution of 2048 x 512 and 64 scans (14 h measuring time).

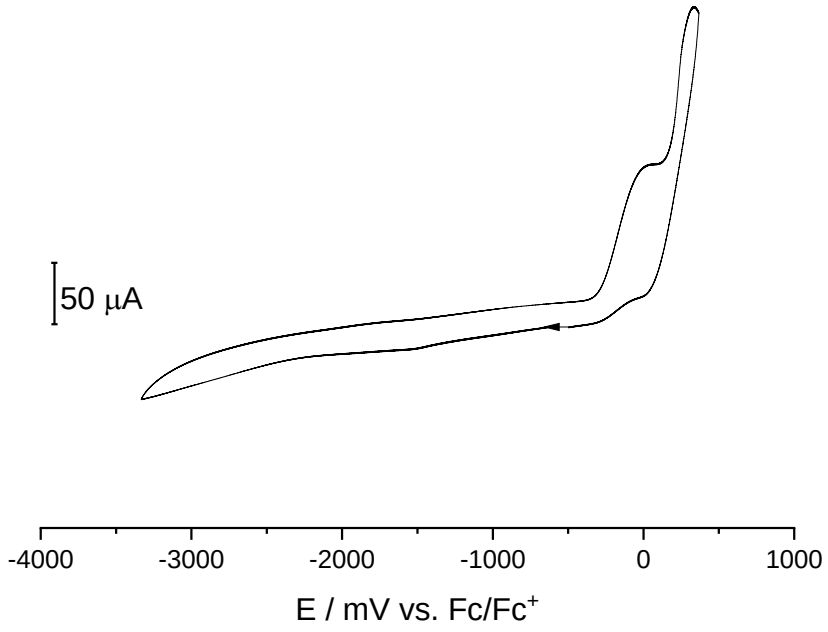

Figure S13 Cyclo voltammogram of 3a in THF vs. Fc/Fc+.

Crystallographic details

The intensity data were collected on a GV-50 diffractometer with TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu-K_α radiation (λ = 1.54184 Å). Data were corrected for Lorentz and polarization effects; analytical absorption corrections were applied to the data.[S8] The structures were solved by direct methods (SHELXT)[S9] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-2018).[S10] All hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystals of **4a** and **5a** contain large voids, filled with disordered solvent molecules. The size of the voids are 310 and

307 Å³/unit cell, respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON[S11] resulting in 54 and 52 electrons/unit cell, respectively. All non-hydrogen atoms were refined anisotropically.[S10] Crystallographic data as well as structure solution and refinement details are summarized in Table S1 of the supplementary information. Olex2 was used for structure representations.[S12]

The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2000854 for **3a**, CCDC-2000855 for **4a**, CCDC-2000856 for **4b**, CCDC-2000857 for **5a**, CCDC-2000858 for **5e**, CCDC-2000859 for **5f**, and CCDC-2000860 for **6b**.

Table S1 Crystal data and refinement details for the X-ray structure determinations.

Compound	**3a**	**4a**	**4b**	**5a**
formula	$C_{52}H_{88}I_2Mg_2N_4$	$C_{72}H_{112}Mg_2N_8$[*	$C_{81}H_{124}Mg_2N_8$	$C_{79}H_{116}Mg_2$
fw (g·mol^{-1})	1135.68	1138.31[*]	1258.49	1282.45[*]
°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	triclinic	triclinic	monoclinic
space group	P 2_1/c	P ī	P ī	P 2_1/c
a/ Å	12.7508(1)	9.8996(2)	12.6943(4)	9.4990(2)
b/ Å	15.3921(1)	12.4467(2)	17.8808(6)	20.0527(3)
c/ Å	14.5516(1)	31.2573(5)	19.6828(4)	19.9097(3)
α/°	90	93.288(1)	107.811(2)	90
β/°	99.728(1)	97.150(1)	105.290(2)	103.793(2)
γ/°	90	108.083(2)	102.834(3)	90
V/Å^3	2814.85(4)	3613.88(12)	3873.6(2)	3683.05(11)
Z	2	2	2	2
ρ (g·cm^{-3})	1.340	1.046[*]	1.079	1.156[*]
μ (cm^{-1})	93.26	6.17[*]	6.18	6.77[*]
measured data	36332	46795	47509	15013
data with I > 2σ(I)	5237	12271	11705	5953
unique data (R_{int})	5684/0.0534	14228/0.0293	15389/0.0542	6449/0.036
wR_2 (all data, on	0.0813	0.0992	0.2245	0.1303
R_1 ($I > 2\sigma(I)$) [a)]	0.0305	0.0373	0.0763	0.0462
S [b)]	1.042	1.035	1.058	1.035
Res. dens./e·Å^{-3}	1.721/-0.705	0.275/-0.318	0.768/-0.724	0.358/-
absorpt method	gaussian	gaussian	gaussian	gaussian
absorpt corr	0.522/0.737	0.936/0.979	0.892/0.966	0.904/0.940
CCDC No.	2000854	2000855	2000856	2000857

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**5e**	**5f**	**6b**
formula	$C_{65}H_{88}Mg_2N_{12}$	$C_{52}H_{68}Mg_2N_{12}$	$C_{74}H_{111}Mg_2N_{12}$
fw ($g \cdot mol^{-1}$)	1086.09	909.80	1217.36
°C	-150(2)	20(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P $2_1/c$	P $2_1/n$	P $2_1/n$
a/ Å	14.3957(5)	9.8229(2)	10.6932(2)
b/ Å	14.0381(5)	10.7632(2)	30.0479(6)
c/ Å	16.1228(7)	23.2089(4)	22.9544(4)
α/°	90	90	90
β/°	113.306(5)	97.157(1)	102.733(2)
γ/°	90	90	90
V/Å^3	2992.4(2)	2434.66(8)	7194.1(2)
Z	2	2	4
ρ ($g \cdot cm^{-3}$)	1.205	1.241	1.124
μ (cm^{-1})	7.48	8.23	6.68
measured data	19636	15403	45537
data with I > 2σ(I)	5123	3831	11838
unique data (R_{int})	5866/0.0364	4242/0.0245	13716/0.0293
wR_2 (all data, on	0.1272	0.0978	0.1136
R_1 ($I > 2\sigma(I)$) [a]	0.0451	0.0375	0.0407
S [b]	1.043	1.031	0.980
Res. dens./$e \cdot Å^{-3}$	0.328/-0.378	0.619/-0.427	0.747/-0.604
absorpt method	gaussian	gaussian	gaussian
absorpt corr	0.695/1.000	0.862/0.906	0.894/0.947
CCDC No.	2000858	2000859	2000860

[*] derived parameters do not contain the contribution of the disordered solvent.

[a] Definition of the *R* indices: $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma |F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + \mathrm{Max}(F_O^2]/3$;

[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

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Preface

The following chapter has already been published in Dalton Transactions of the Royal Society of Chemistry.

'Ditopic bis(N,N',N'-substituted 1,2-ethanediamine) ligands: synthesis and coordination chemistry´ *Dalton Trans.* **2020**, *49*, 13818-13828.

Authors

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Author contributions

The manuscript was prepared by the first author (A. Rösch). R. Kretschmer supervised the research and revised the manuscript. All ligands were isolated and characterized (NMR, MS) by C. M. Herzog. All Al-complexes were first isolated by C. M. Herzog and in equal measure characterized and resynthesized by A. Rösch and C. M. Herzog. S.H.F. Schreiner assisted with the resynthesis of some complexes. All further complexes were isolated and characterized (NMR, IR, EA, X-Ray) by the first author. VT ^{1}H NMR spectra were measured at the NMR Department of the University of Regensburg, for which the first author prepared the samples. H. Görls evaluated the single crystal X-Ray diffraction measurements and provided the corresponding section in the Supporting Information.

Acknowledgement

The work is dedicated to Winfried Plass on the occasion of his 60th birthday. The project was financially supported by the Deutsche Forschungsgemeinschaft (DFG, KR4782/3-1), the Friedrich Schiller University Jena and the *Elite Network of Bavaria*. We thank the reviewers for valuable comments and suggestions.

4. Ditopic bis(N,N′,N′-substituted 1,2-ethanediamine) ligands: synthesis and coordination chemistry

Abstract

*The synthesis of two different types of bis(*N,N′,N′*-substituted 1,2-ethanediamine)s, bridged either through the secondary (type **1**) or tertiary (type **2**) amine groups is reported. Selected protio-ligands have been applied in subsequent metallation reactions using aluminium, magnesium, tin, and zinc sources allowing to isolate five mononuclear and eight dinuclear complexes. All complexes have been fully characterized and their solid-state structures have been studied by means of single-crystal X-ray diffraction analysis. Nine of the 13 complexes carry reactive alkyl, amide or hydride groups, which indicates their potential as catalysts or supports for (transition) metals.*

4.1 Introduction

Ligands possessing two binding sites play a pivotal role in modern coordination chemistry as they grant access to mono-, di- and polynuclear species from all sections of the periodic table.[1] As multidentate chelates, they give rise to stable mononuclear metal complexes and allow controlling the steric constraints with respect to both, shielding of the metal centre and adjusting the stereochemical properties of the thus formed complex. Furthermore, these ditopic ligands also offer the advantage of bringing two and sometimes more metal centres in close proximity. With respect to catalysis, dinuclear complexes allow cooperative or synergistic effects to arise[2] and framing two metals within a single molecule avoids ill-defined monomer/dimer equilibria. Hence, such complexes regularly excel their mononuclear counterparts in terms of reactivity and selectivity and allow achieving reactions that are not accessible with complexes possessing only one metal centre. In this regard, selecting appropriate ligands is crucial and even small changes with respect to electronic

and/or steric implications may have a significant impact on the coordination behaviour. In main-group chemistry, which attracted much interest within the last decades,[3] two ligand classes received particular attention: bis(N-heterocyclic carbene)s[4] and *N*,*N*-dinucleating ligands.[1h] With respect to the latter, bis(amidine)s (**A**)[5] have been frequently used and noticeable effort has been directed towards bis(guanidine)s (**B**)[6] and bis(β-diketimine)s (**C**),[7]Fig. 1. However, the redox activity and non-innocence is well document for β-diketimines[8] and related ligands and ligand-centered side reactions have also been reported for bis(β-diketiminate) complexes.[7r] The saturated backbone of *N*,*N*',*N*'-substituted 1,2-ethanediamines (**D**) prevents conjugation and hence delocalization,[9] which makes the related bis(*N*,*N*',*N*'-substituted 1,2-ethanediamine)s interesting targets for ligand design. Due to the asymmetric nature of *N*,*N*',*N*'-substituted 1,2-ethanediamines, bridging is either achieved through the secondary or tertiary amine groups giving rise to protio-ligands of type **1** and **2**, respectively, Fig. 1.

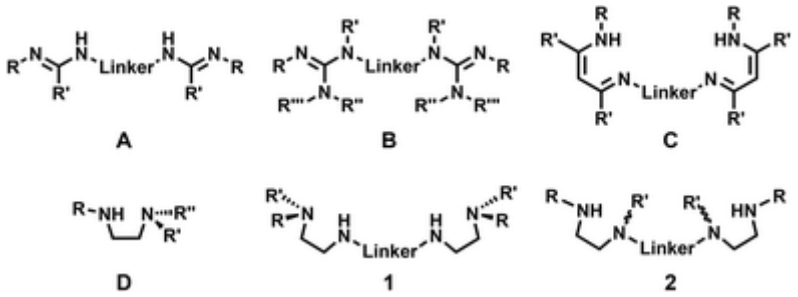


Fig. 1 Bis(amidine)s (**A**), bis(guanidine)s (**B**), bis(β-diketimine)s (**C**), *N*,*N*',*N*'-substituted 1,2-ethanediamines (**D**), and bis(amidoamine)s of type **1** and **2** reported herein.

In 2003, the group of Hagadorn reported about the first example of a type **1** bis(*N*,*N*',*N*'-substituted 1,2-ethanediamine) containing a dibenzofuran-bridge.[10] Notably, the authors defined the new ligand class as bis(amidoamine)s and as this notation has been adopted in the literature, we will also make use of it in the following. Although, the related dinuclear metal complexes showed remarkable reactivity and catalytic activity,[10,11] no further investigations with respect to the ligand itself have been reported. However, its non-

innocence in terms of hydride abstraction from a methylene group by forming a C=N double bond was observed when treating dinuclear zinc enolate complexes with tris(pentafluorophenyl)borane.[11c] As such a kind of reactivity was previously observed for *N*,*N*-alkylated anilines,[12] this behavior might be due to the aromatic linker group and could be avoided by using alternative bridging units. In addition, type **2** bis(amidoamine)s have no precedence in the literature. Hence, we set out to synthesize new bis(amidoamine)s of type **1** and **2** and investigated their reactivity towards aluminium, magnesium, tin, and zinc precursors. Our findings are reported herein.

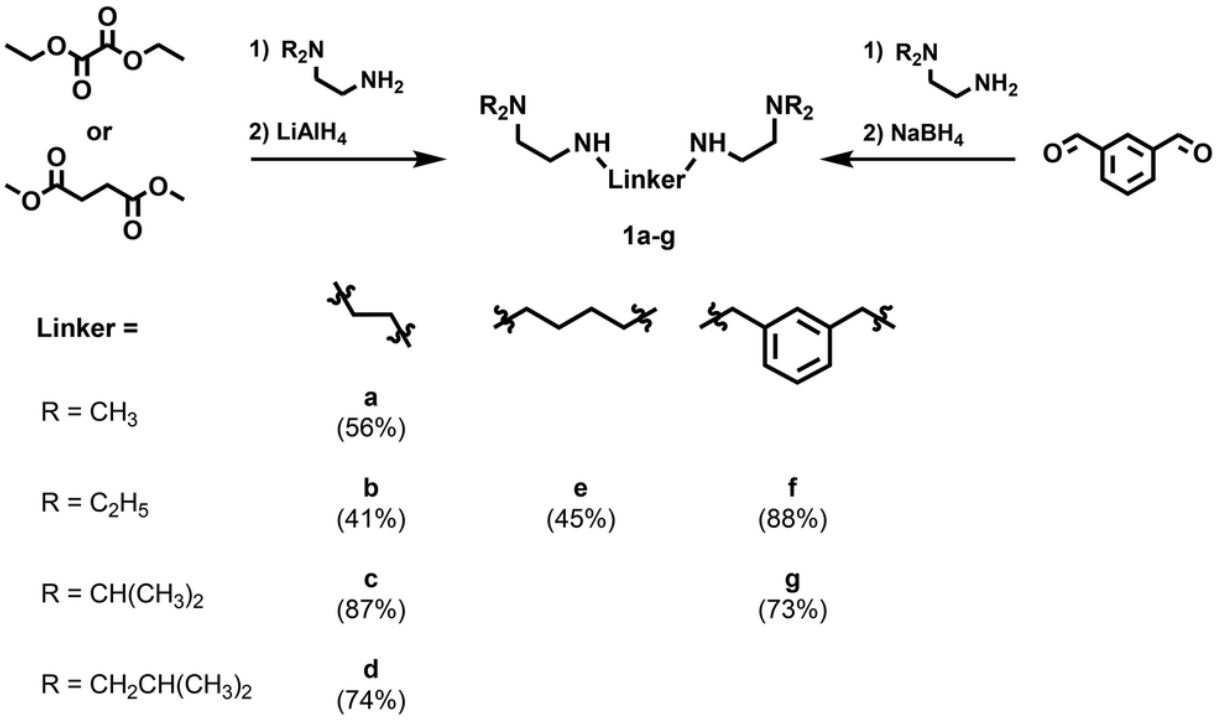
4.2 Results and discussion

Protio-ligand synthesis

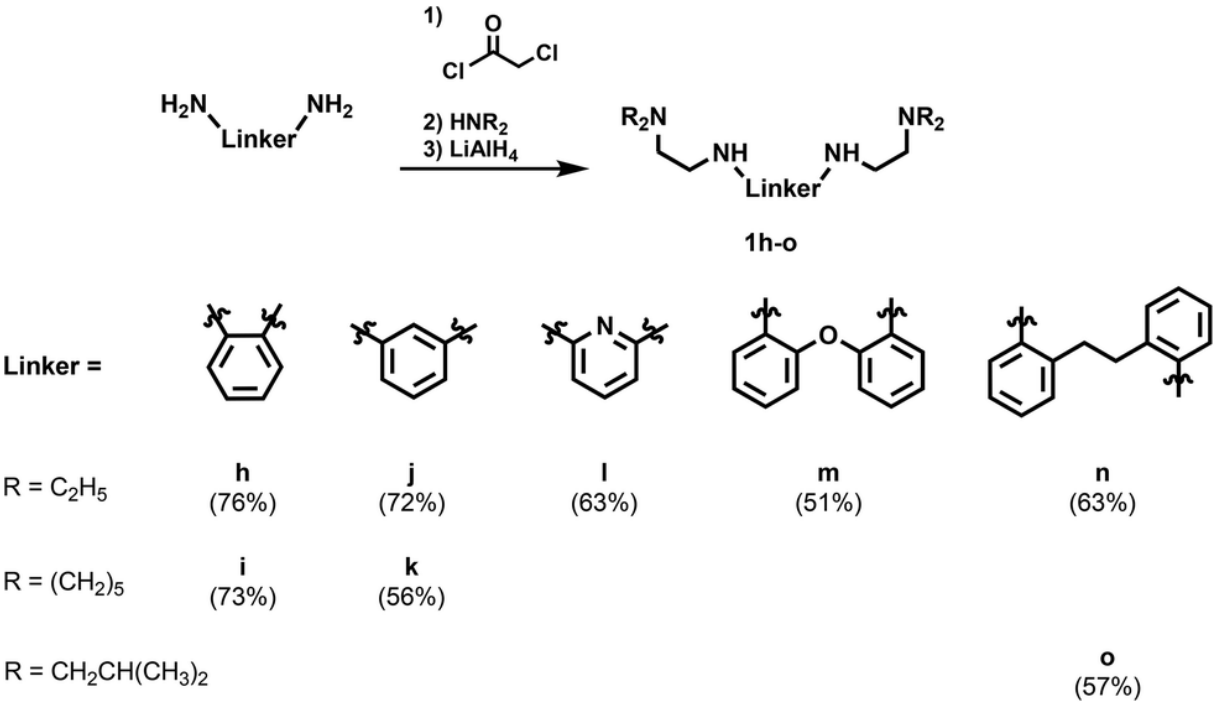
The only yet reported dibenzofuran-bridged type **1** bis(amido-amine)s have been synthesized by the copper-catalyzed coupling of 4,6-diiodibenzofurane and alkylated ethylene-diamines.[10,11a] As this approach is limited to aromatic linker groups, we established alternative synthetic protocols towards the bis(amidoamine)s **1** and **2**, respectively, which will be discussed consecutively in the following.[13]

With respect to type **1** bis(amidoamine)s possessing terminal tertiary and lateral secondary amine functions, two general approaches have been applied, Schemes 1 and 2. The first one originates from *N*,*N*-substituted ethylene diamines and a dicarbonyl precursor, *i.e.*, diethyl oxalate, dimethyl succinate and isophthalaldehyde. The thus formed amides and imines were subsequently reduced using $LiAlH_4$ and $NaBH_4$, respectively, affording the ethylene, butylene, and 1,3-xylylene bridged bis(amidoamine)s **1a–g** in yields ranging from 41 to 88%. The second approach starts from aromatic diamines that are converted first to the respective bis(α-haloamide)s by using chloro acetylchloride.

Nucleophilic substitution of the halide with aliphatic secondary amines and reduction using lithium aluminium hydride allowed to isolate the bis(amidoamine)s **1h–o** in yields between 51 and 76%.

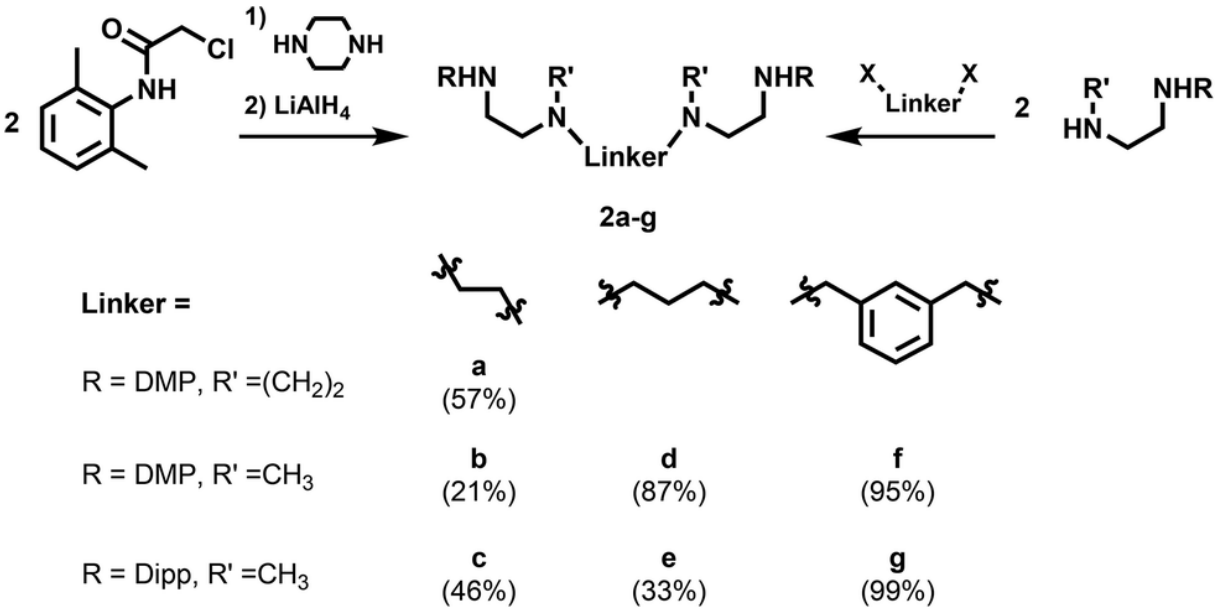


Scheme 1 Synthesis of bis(amidoamine)s of type **1** starting from dicarbonyl precursors.



Scheme 2 Synthesis of bis(amidoamine)s of type **1** from primary diamines.

Bis(amidoamine)s of type **2**, which are bridged through the tertiary instead of the secondary amine, are also synthesized *via* two routes, Scheme 3. The piperazine-bridged compound **2a** is obtained in 52% yield by reacting piperazine with an α-chloroanilide and subsequent reduction using $LiAlH_4$. The acyclic species **2b–g**, however, were alternatively synthesized from *N*-methyl-*N*'-aryl substituted ethylenediamines and a suitable dihalide and obtained in yields ranging from 21 to 99%.



Scheme 3 Synthesis of bis(amidoamine)s of type **2**. DMP = 2,6-dimethylphenyl, Dipp = 2,6-diisopropylphenyl, X = Br, Cl.

The ^{1}H NMR spectra of the protio-ligands in $CDCl_3$ have the expected pattern characteristic for a symmetric or averaged structure in solution. In order to elucidate the situation in the solid state, single-crystals of **2a** and **2b**, suitable for an X-ray diffraction analysis could be obtained. Their molecular structures are shown in Fig. 2. In brief, the piperazine unit within **2a** possesses the expected chair conformation and the two binding pockets occupy the equatorial positions while directing in opposite directions, a behaviour well known for other piperazine-bridged ligands.[14] In **2b**, the two binding pockets are also directed away from each other. Both species feature comparable N–C–C–N dihedral angles of 55.79(12) to 59.11(12)° as well as C–N bond lengths in between 1.4629(16) and 1.4682(16) Å, which are in good agreement with values of the related *N*,*N*′,*N*′-substituted 1,2-ethane-diamines (55.65(12)° and 1.4627(15)–1.4637(13) Å).[9a]

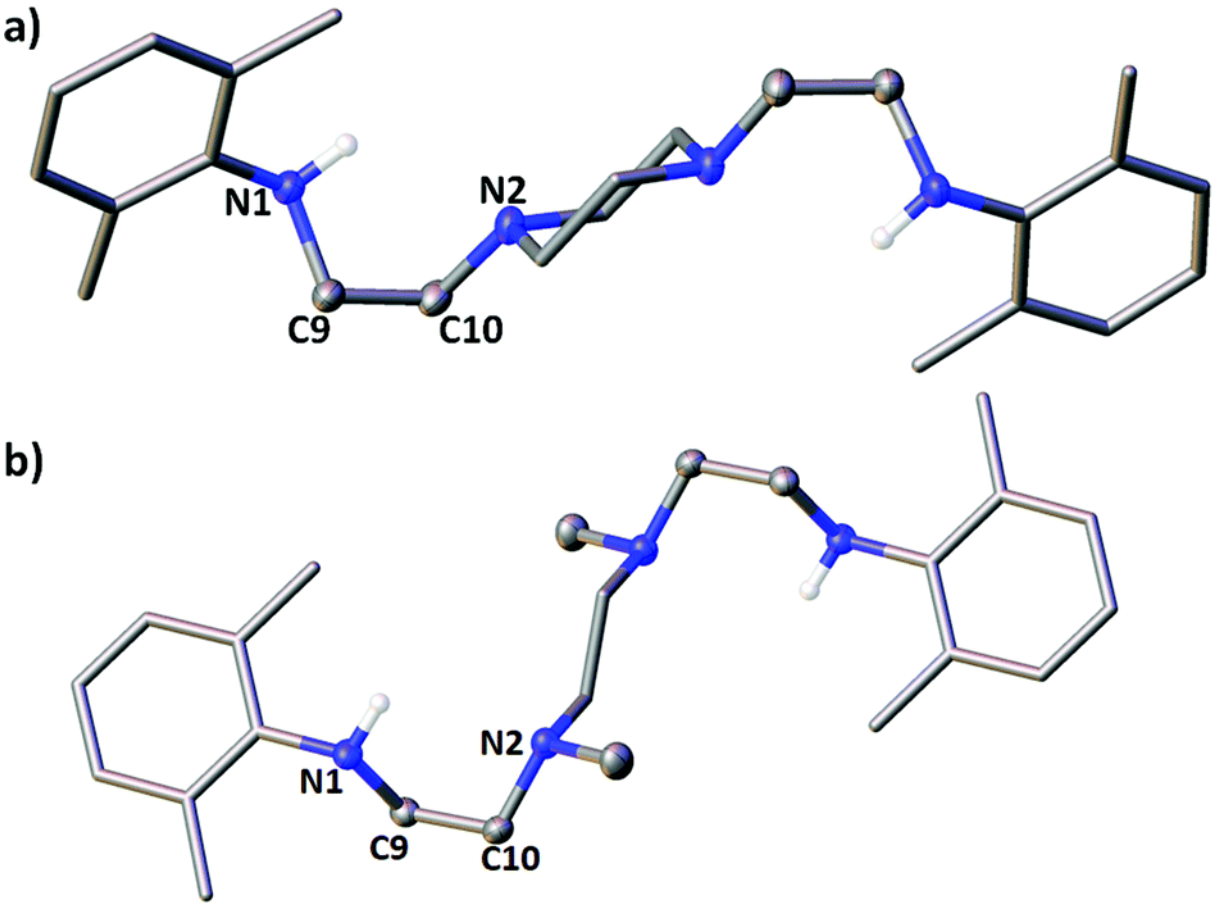


Fig. 2 Solid-state structures (hydrogen atoms except the NH are omitted for clarity) with selected bond lengths [Å]: (a) **2a**: N1–C9 1.4682(16), C9–C10 1.5221(19), N2–C10 1.4629(16); (b) **2b**: N1–C9 1.4675(14), C9–C10 1.5188(12), N2–C10 1.4657(14).

Synthesis and structural characterization of mono- and dinuclear complexes

The stereochemistry of the mono- and dinuclear complexes originating from the protio-ligands of type **1** and **2** is significantly affected by the way both binding pockets are connected. Upon complexation, rapid inversion of the nitrogen atom of the tertiary amine is effectively cancelled out locking the overall configuration. In case of the protio-ligands **1a–n** this does not affect the overall stereochemistry of the thereby formed mono- and dinuclear complexes, Fig. 3. Complexation of the protio-ligands **2b–g**, however, gives rise to two chiral nitrogen-donor atoms and possibly induces the formation of several

diastereomers. The ethylene-bridge was chosen as an example assuming R' having the lowest Cahn–Ingold–Prelog-priority.

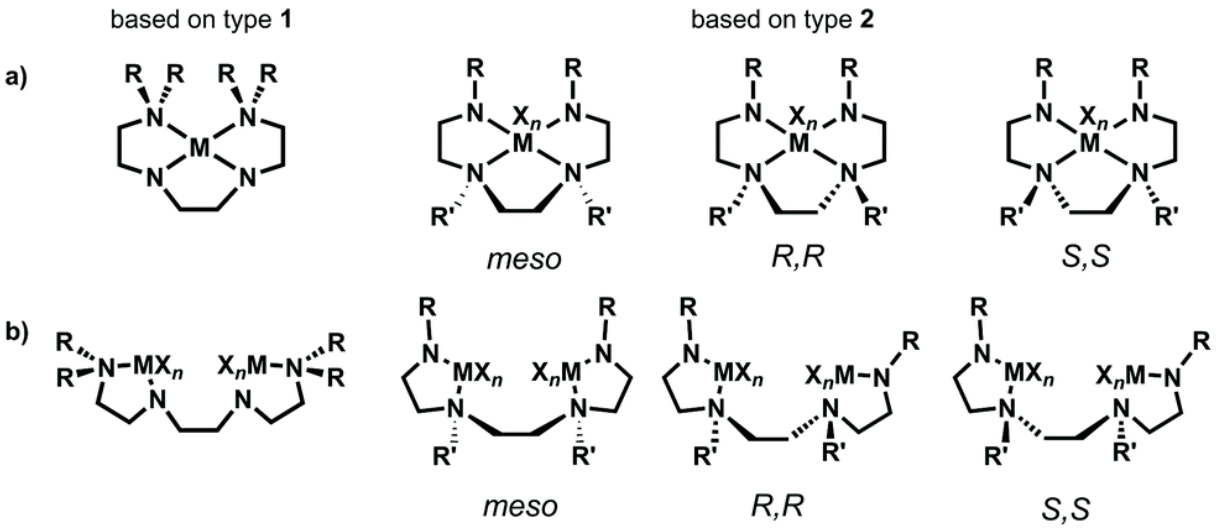
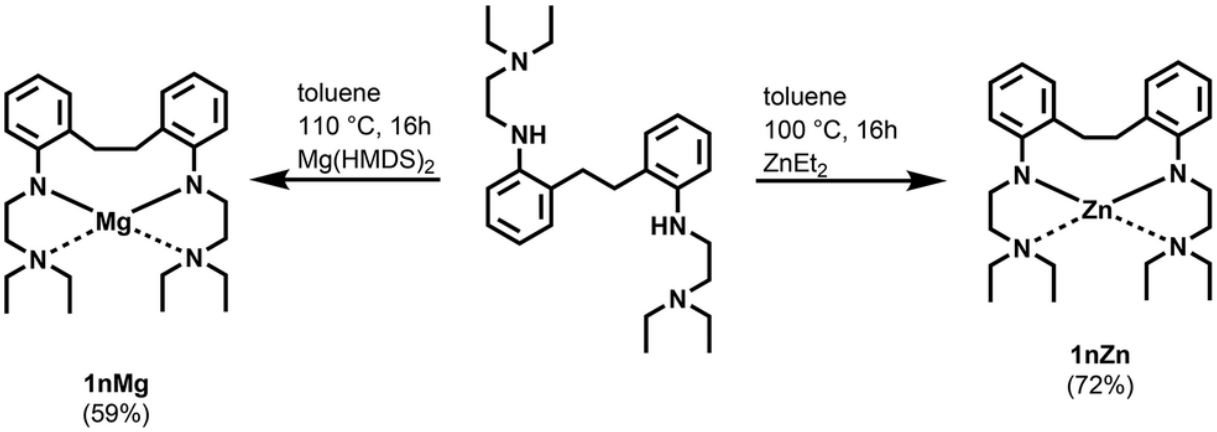


Fig. 3 Coordination modes of (a) mono- and (b) dinuclear complexes originating from the protio-ligands **1** and **2**, respectively.

While repeated attempts to obtain magnesium or zinc complexes starting from the protio-ligand **1m** remained unsuccessful, we were able to isolate well-defined compounds using **1n**, Scheme 4. In detail, **1nMg** was obtained by using magnesium bis[bis(trimethylsilyl)amide] while diethyl zinc was used to synthesize the respective zinc complex **1nZn**. Both complexes could be isolated as colourless crystals, which were suitable for X-ray diffraction (XRD) analyses and their molecular structures in the solid state are shown in Fig. 4; **1nZn** crystallizes as two independent molecules, which differ in their conformation, Fig. S1.† Within the homoleptic complexes **1nMg** and **1nZn**, the metal centre is four-fold-coordinated by the two *N*,*N*-chelates. As expected, the dative M–N1 and M–N4 bonds (Mg: 2.1679(14) and 2.1731(14) Å; Zn: 2.1685(12) and 2.1690(13) Å) are longer compared to the normal M–N2 and M–N3 bonds by about 0.16 (Mg) and 0.23 Å (Zn). Notably, only the normal bonds are significantly affected by the central atom, with shorter bond lengths in case of zinc (1.9383(13) and 1.9448(14) Å) as compared to magnesium (2.0071(15) and 2.0112(14) Å). The N–M–N bite angles, finally, remain by and large

unaffected by the central metal, *i.e.*, 82.95(5) and 83.5(6)° in case of magnesium and 83.69(5) and 84.59(5)° for zinc. Notably, anagostic Mg···HC interactions (2.3324(5) and 2.3667(5) Å) with the methylene unit of the backbone are observed, while the contacts are significant longer in case of **1nZn** (2.4260(3) and 2.4391(4) Å).



Scheme 4 Deprotonation of **1n** by magnesium bis[bis(trimethylsilyl)amide] or diethyl zinc.

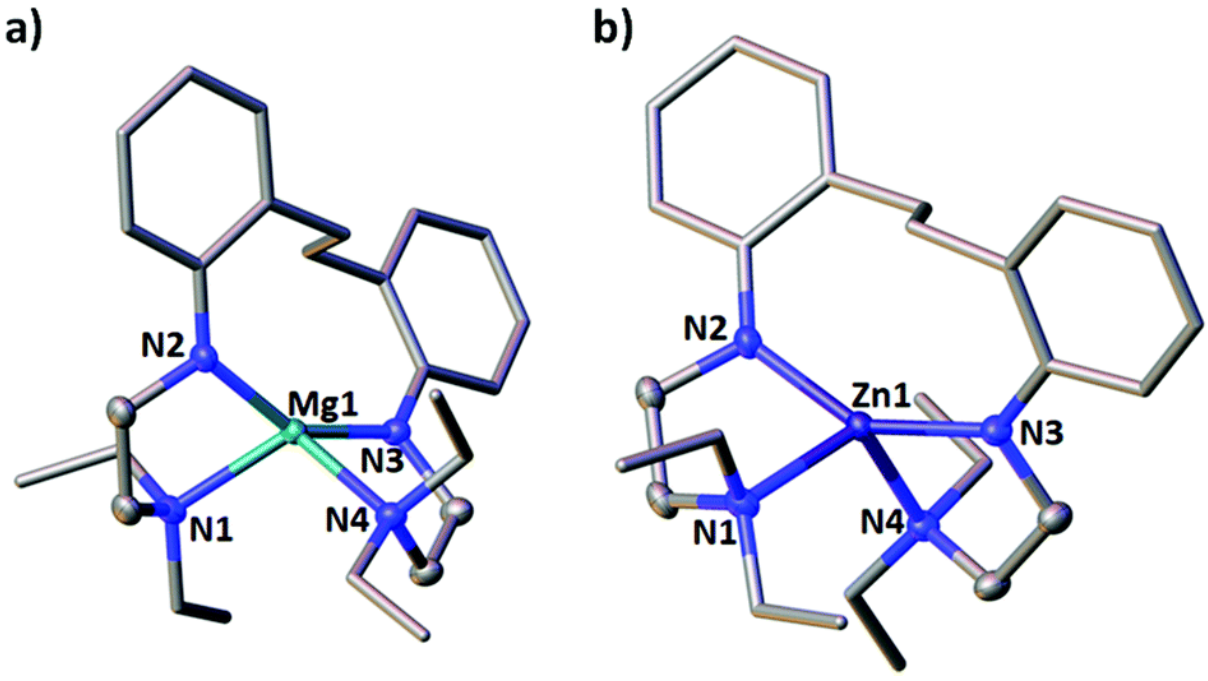


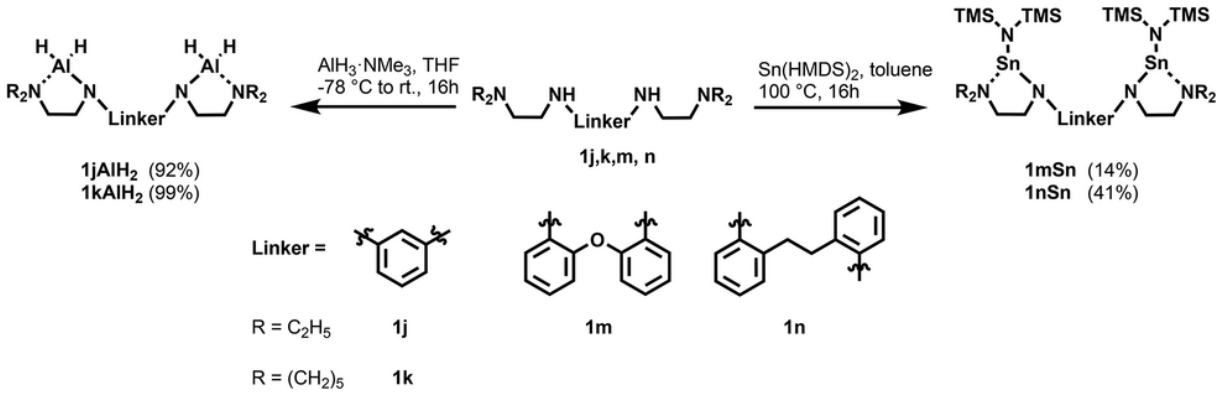
Fig. 4 Solid-state structures (hydrogen atoms except those of the anagostic bonds are omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **1nMg**: Mg1–N1 2.1679(14), Mg1–N2 2.0071(15), Mg1–N3 2.0112(14), Mg1–N4 2.1731(14), N1–Mg1–N2 83.55(6), N1–Mg1–N3 115.0866(8), N1–Mg1–N4 111.1091(7), N2–Mg1–N3 148.36256(7), N2–Mg1–N4

115.3234(9), N3–Mg1–N4 82.95(5); (b) **1nZn**: Zn1–N1 2.1685(12), Zn1–N2 1.9448(14), Zn1–N3 1.9383(13), Zn1–N4 2.1690(13), N1–Zn1–N2 83.69(5), N1–Zn1–N3 116.3320(4), N1–Zn1–N4 110.8010(8), N2–Zn1–N3 146.9457(2), N2–Zn1–N4 113.9624(4), N3–Zn1–N4 84.59(5).

The behaviour in solution differs for both complexes. In case of **1nMg**, a complex pattern of sharp resonances indicates a species of low symmetry. Notably, the number of resonances is strongly solvent-dependent and increases in going from THF-d_8 to C_6D_6. In the former case, one triplet and one quartet account for the terminal ethyl substituents, while they are split into two triplets and two quartets in C_6D_6 solution. The same holds true for the methylene groups of both, the ligands' backbone and the bridge which appear as three and six multiplets in THF-d_8 and in C_6D_6, respectively. **1nZn** was only soluble in a mixture of THF-d_8 and C_6D_6 and the ^{1}H NMR spectrum features broadened resonances for the ethyl groups, indicating slow conformational exchange at room temperature on the NMR time scale, while well-resolved signals were observed for the protons of both, the methylene units and the aromatic ring. The latter finding is consistent with a pseudo C_2-symmetric structure of the ligand framework in solution.

We next became interested if dinuclear aluminium(III) and tin(II) complexes are accessible starting from the protio-ligands **1**. Hence, **1j** and **1k** were allowed to react with aluminium hydride trimethylamine, while **1m** and **1n** were treated with tin bis[bis(trimethylsilyl)amide], Scheme 5. Please note that the reactions of **1a** and **1d** with $Sn(HMDS)_2$ yielded only a complex reaction mixture. The dinuclear aluminium(III) hydride complexes **1jAlH$_2$** and **1kAlH$_2$** were obtained in excellent yields of 92% and 99%, respectively. Although we could also isolate the dinuclear tin(II) complexes **1mSnHMDS** and **1nSnHMDS**, the yields were significantly lower (14 and 41%, respectively). As all four compounds were isolated as crystalline material, an XRD analysis allowed to derive their molecular solid-state structures, which are shown in Fig. 5 and 6. **1jAlH$_2$** and **1kAlH$_2$** feature two tetra-coordinated aluminium centres that are facing away from eachother. The Al1–N1 and Al1–N2 bond lengths of both compounds are comparable and resemble values of aluminium complexes of *N*,*N*',*N*'-substituted 1,2-ethanediamine ligands.[9a] The Al–H bond lengths (1.516(15)–1.56(2) Å) and H–Al–H bond

angles (109.6(12) and 119.5(11)°) are reminiscent of values reported before for mononuclear aluminium dihydride complexes based on *N*,*N*-chelating ligands (1.379(45)–1.611(19) Å; 109.4(16)–122(2)°).[15] The room temperature ^{1}H NMR spectra **1jAlH$_2$** and **1kAlH$_2$** in $CDCl_3$ are distinctly different: in the first case, a simple set of resonances, *i.e.* one triplet and quartet representing the terminal ethyl rests but also the expected singlet : doublet : triplet pattern of the aryl-bridge, account for a symmetric or averaged structure in solution. In case of **1kAlH$_2$**, however, a series of sharp multiplets including the resonances of the 1,3-phenylene-bridge indicate the presence of at least two conformers that do not undergo rapid exchange. The presence of an AlH_2 group was established by ^{1}H NMR spectroscopy and the AlH_2 resonances appear as broad singlets at 3.90 and 3.97 ppm, respectively. Further evidence is given by the asymmetric and symmetric Al–H stretches that occur at 1780 and 1808 cm^{-1} as well as 1775 and 1805 cm^{-1}. The mean values, *i.e.*, 1794 and 1790 cm^{-1}, are significantly red-shifted compared to aluminium hydrides based on other *N*,*N*-chelating ligands.[6i,16]



Scheme 5 Synthesis of dinuclear aluminium(III) and tin(II) complexes.

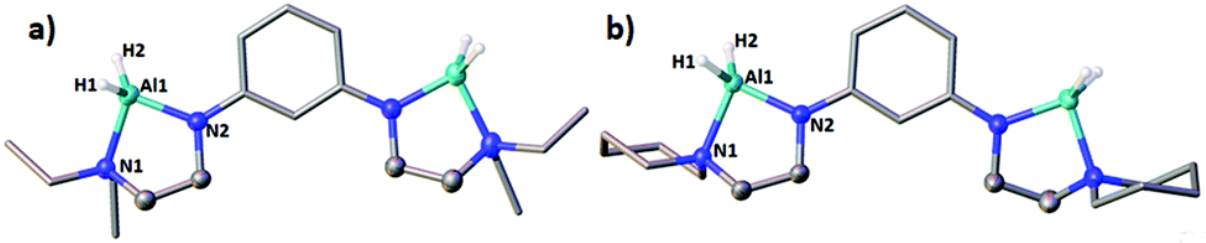


Fig. 5 Solid-state structures (hydrogen atoms except the AlH and cocrystallized THF in case of **1kAlH$_2$** are omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **1jAlH$_2$**: Al1–N1 1.9972(12), Al1–N2 1.8479(15), Al1–H1 1.54 (2), Al1–H2 1.516(15), N1–Al1–N2 87.40(5), H1–Al1–H2 119.5(11); (b) **1kAlH$_2$**: Al1–N1 2.0042(14), Al1–N2 1.8473(14), Al1–H1 1.56(2), Al1–H2 1.54(2), N1–Al1–N2 88.80(6), H1–Al1–H2 113.7(12).

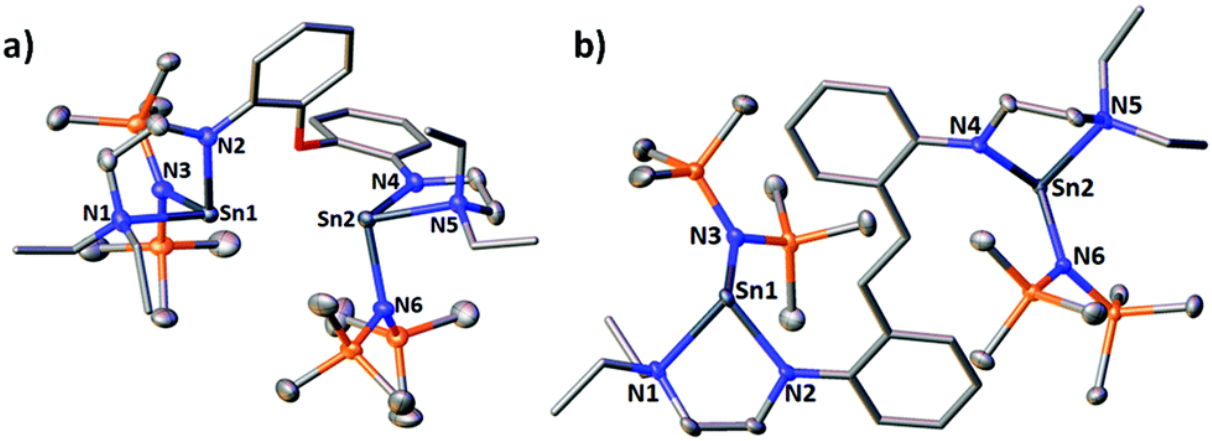


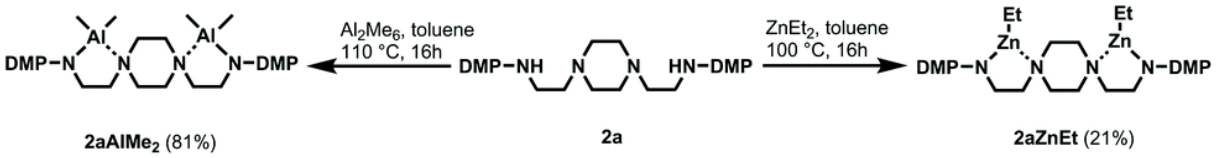
Fig. 6 Solid-state structures (hydrogen atoms are omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **1mSnHMDS**: Sn1–N1 2.453(3), Sn1–N2 2.139(2), Sn1–N3 2.154(3), Sn2–N4 2.165(2), Sn2–N5 2.374(3), Sn2–N6 2.165(3), N1–Sn1–N2 75.58(9), N4–Sn2–N5 76.07(9); (b) **1nSnHMDS**: Sn1–N1 2.3904(18), Sn1–N2 2.1690(18), Sn1–N3 2.1520(17), Sn2–N4 2.1513(16), Sn2–N5 2.3666(17), Sn2–N6 2.1440(17), N1–Sn1–N2 79.27(6), N4–Sn2–N5 78.32(6).

Within the distannylenes **1mSnHMDS** and **1nSnHMDS** the tin(II) centres are surrounded by an overall pyramidal ligand array and reside in a distorted tetrahedral environment with one vertex occupied by a stereo-chemically active lone pair of electrons, Fig. 6. The Sn–N(TMS)$_2$ bond lengths (2.1440(17)–2.165(3) Å) are in good agreement with those reported of related mono- (2.109(4)–2.150(2) Å)[17] and distannylenes (2.124(2)–2.140(5) Å)[18] involving *N*,*N*-chelating ligands. The room temperature ^{1}H NMR spectrum of **1mSnHMDS** in toluene-d$_8$ consists of a series of broad resonances that eventually collapse upon heating to 353 K to well-defined signals being in agreement with a symmetric or

averaged structure in solution. This indicates hindered motion of the molecule likely due to the more rigid oxydiphenylene-bridge. In contrast, the resonance sets of **1nSnHMDS** in C_6D_6 are symmetrical due to conformational averaging on the NMR time scale illustrating the increased flexibility of the bridging group.

After having studied the coordination behaviour of the protio-ligands **1**, we became interested in the complexation abilities of **2**. As discussed above, the coordination of the lateral tertiary nitrogen atoms induces chirality and possibly leads to various diastereomers, Fig. 3. **2a** possesses a bridging piperazine ring and the two lateral nitrogen atoms do not become chiral upon complexation. However, two isomers, *i.e.*, *anti* and *syn*, are conceivable when assuming a chair conformation of the central piperazine ring.

Reacting **2a** with trimethylaluminium or diethyl zinc affords the complexes **2aAlMe$_2$** and **2aZnEt** in 81% and 21% yield, respectively, as colourless crystals, Scheme 6. Their molecular structures in the solid state are given in Fig. 7 and as expected, both complexes exist in the *anti*-configuration, *i.e.*, both binding sites are directed in opposite directions. The structural parameters including the Al–N (1.8361(13) and 2.0723(13) Å) and Al–C (1.9680(17)–1.9722(16) Å) bond lengths of **2aAlMe$_2$** are comparable to those of the related mononuclear counterpart.[9a] While for **2aZnEt** no related mononuclear relative has so far been reported, the Zn–C bond lengths (1.958(2)–1.972(2) Å) are in good agreement with values reported for comparable mononuclear complexes based on *N*,*N*-chelating ligands (1.964(5)–2.002(2) Å).[19]



2aAlMe$_2$ (81%) **2a** **2aZnEt** (21%)

Scheme 6 Synthesis of dinuclear aluminium(III) and zinc(II) complexes starting from **2a**.

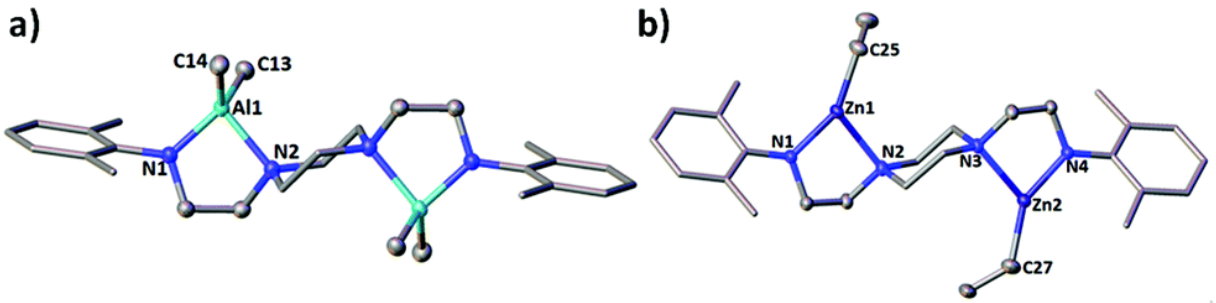
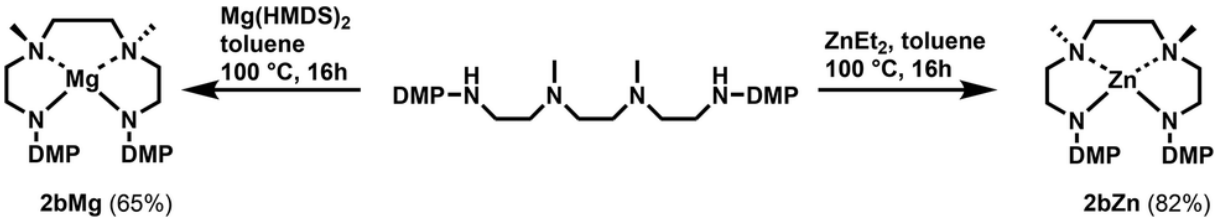


Fig. 7 Solid-state structures (hydrogen atoms are omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **2aAlMe$_2$**: Al1–N1 1.8361(13), Al1–N2 2.0723(13), Al1–C13 1.9722(16), Al1–C14 1.9680(17), N1–Al1–N2 87.35(5), C13–Al1–C14 113.28(7); (b) **2aZnEt**: Zn1–N1 1.8920(17), Zn1–N2 2.2060(12), Zn1–C25 1.972(2), Zn2–N3 2.1842(12), Zn2–N4 1.8966(17), Zn2–C27 1.958(2), N1–Zn1–N2 85.33(6), N3–Zn2–N4 85.27(6).

In going from **2a** to the more flexible protio-ligand **2b**, the reaction with diethyl zinc does not afford a heteroleptic dinuclear complex but instead the mononuclear homoleptic complex **2bZn** is formed in 82% yield, Scheme 7. As expected, the same holds true for the reaction of **2b** with magnesium bis[bis(trimethylsilyl)amide], which gives rise to **2bMg** (65% yield). Single crystals of both compounds could be obtained and their molecular structures have been investigated by an XRD analysis, Fig. 8.



Scheme 7 Synthesis of homoleptic magnesium and zinc complexes starting from **2b**.

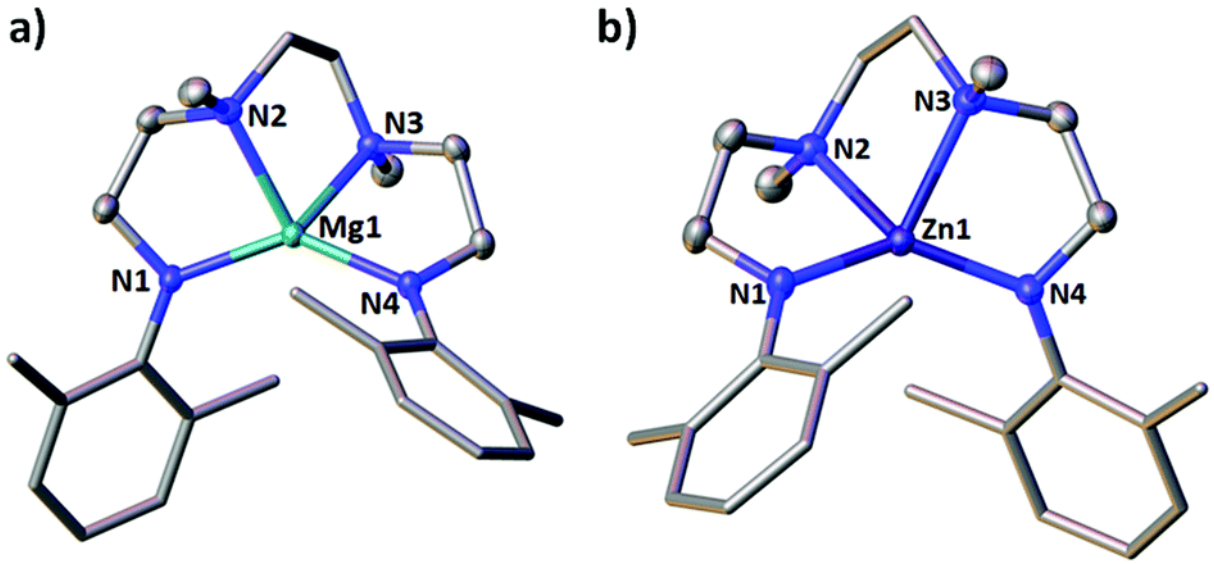
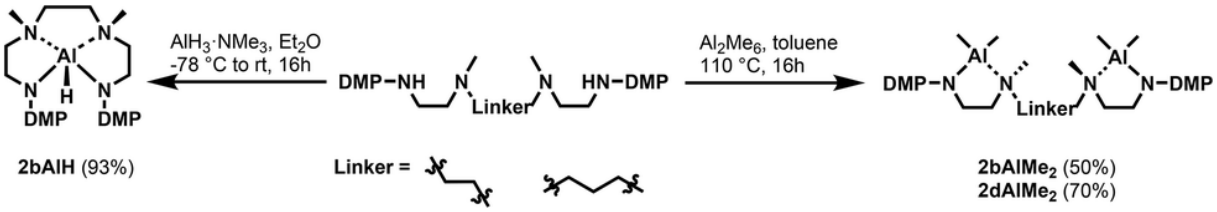


Fig. 8 Solid-state structures (hydrogen atoms are omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **2bMg**: Mg1–N1 2.0027(9), Mg1–N2 2.1781(10), Mg1–N3 2.1968(10), Mg1–N4 2.0009(8), N1–Mg1–N2 85.42(4), N3–Mg1–N4 85.89(4); (b) **2bZn**: Zn1–N1 1.9291(13), Zn1–N2 2.1882(12), Zn1–N3 2.2091(11), Zn1–N4 1.9281(13), N1–Zn1–N2 85.81(5), N3–Zn1–N4 86.49(5).

2bMg and **2bZn** crystallize in the centrosymmetric space groups $P2_1/c$ and $P2_1/n$, respectively, and accommodate hence equal numbers of the *R*,*R*- and *S*,*S*-diastereomers. While the obtained molecular structures do not allow deducing information of the bulk sample, ^{1}H NMR spectroscopic data (measured in THF-d_8 and in C_6D_6/THF-d_8, respectively) give no evidence for the presence of the *meso*-diastereomer. Characteristic features are two singlets integrating for 12 and 6 protons, respectively, accounting for the methyl groups at the 2,6-DMP substituent and at the lateral nitrogen atoms. The latter resonance is significantly affected by the central metal and appears at 2.59 ppm in case of magnesium while it is shifted to higher field in case of zinc (2.14 ppm). The methylene resonances of the formed macrocycle split into several multiplets indicating separate signals for the axial and equatorial protons. Furthermore and due to anisotropic effects, the axial protons show smaller chemical shift values compared to their equatorial counterparts. The Mg–N and Zn–N bond lengths with values of 2.0009(8) to 2.1968(10) Å and 1.9281(13) to 2.2091(11) Å, respectively, as well as the N–M–N bite angles (85.42(4) and 85.89(4)° (Mg) and 85.81(5) and 86.49(5)° (Zn)) resemble those of the mononuclear complexes **1nMg** and **1nZn** discussed

before. However, the shorter ethylene-bridge in case of **2bMg** and **2bZn** induces wider NMN plane to plane twist angles (118.73(4) and 118.12(4)°, respectively) as compared to the related complexes of **1n** (99.17(6) and 98.75(5)° for **1nMg** and **1nZn**, respectively).

Reacting the protio-ligand **2b** with aluminium hydride trimethylamine yields the mononuclear complex **2bAlH**, regardless of whether one or two equivalents of $AlH_3{\cdot}NMe_3$ were used, Scheme 8. Its molecular solid-state structure has been analysed by single-crystal XRD revealing the presence of the *meso*-diastereomer and the two NCH_3 groups and the hydride ligand are oriented in the same direction, Fig. 9a. The ^1H NMR spectrum recorded in C_6D_6 shows two singlets for the DMP methyl groups indicating hindered rotation about the N–C_{aryl} bond. One singlet accounts for the methyl groups bound to the lateral nitrogen atoms while the resonances of the linkers' methylene groups appear a several multiplets in agreement with a locked conformation of the macrocycle. The Al–N bonds (1.8520(11) to 2.3482(13) Å) are in the range of the dinuclear complexes **1jAlH₂** and **1kAlH₂** discussed above. The Al–H bond length (1.522(17) Å) is in good agreement with values reported before for other aluminium(III) monohydride complexes involving four Al–N bonds (1.48(4) to 1.607(15) Å).[20] The Al–H stretching frequency of 1735 cm^{-1} falls well in between previously reported values of 1693 to 1836 cm^{-1}.[20b,d,21]



Scheme 8 Synthesis of mono- and dinuclear aluminium complexes.

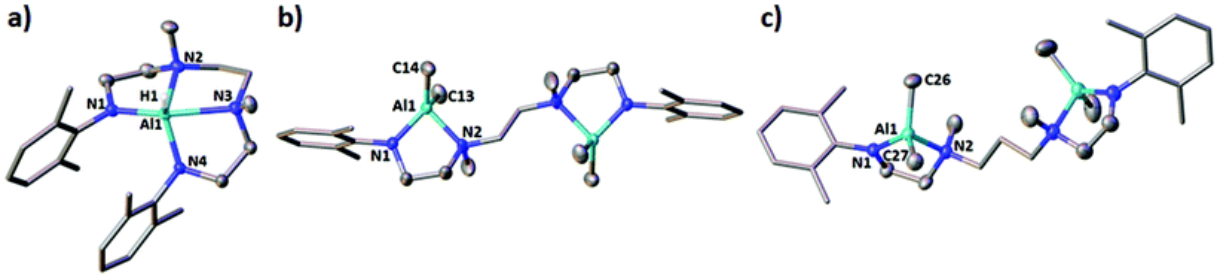


Fig. 9 Solid-state structures (hydrogen atoms except the AlH and in case of **2bAlMe₂** a second independent molecule are

omitted for clarity) with selected bond lengths [Å] and angles [°]: (a) **2bAlH**: Al1–N1 1.8924(13), Al1–N2 2.0771(11), Al1–N3 2.3482(13), Al1–N4 1.8520(11), Al1–H1 1.522(17), N1–Al1–N2 83.17(5), N3–Al1–N4 79.31(5); (b) **2bAlMe$_2$**: Al1–N1 1.8324(16), Al1–N2 2.021(10), Al1–C13 1.984(6), Al1–C14 1.939(8), N1–Al1–N2 87.0(2), C13–Al1–C14 114.7(3); (c) **2dAlMe$_2$**: Al1–N1 1.8352(14), Al1–N2 2.0400(16), Al1–C26 1.975(2), Al1–C27 1.9759(19), N1–Al1–N2 87.21(6), C26–Al1–C27 114.09(9).

Changing the aluminium source to trimethyl aluminium does not afford the respective mononuclear complex but instead the dinuclear aluminium alkyl complex **2bAlMe$_2$** is formed in 50% yield. The same holds true for the propylene-bridged protio-ligand **2d**, which affords the dinuclear complex **2dAlMe$_2$** in 70% yield. Their molecular structures in the solid state are shown in Fig. 9. In case of **2bAlMe$_2$**, the *meso*-diastereomer was observed by XRD, while in case of **2dAlMe$_2$** the *S*,*S*-diastereomer was detected, but the centrosymmetric $P2_1/c$ space group indicates that **2dAlMe$_2$** is obtained as a mixture of enantiomers. Please note, that increasing the lengths of the linker group changes the priorities according to the Cahn–Ingold–Prelog priority rules although **2bAlMe$_2$** and **2dAlMe$_2$** are virtually identical.[22] Both species possess two tetra-coordinated aluminium centres. The Al–C and Al–N bond lengths (1.939(8)–1.984(6) Å and 1.8302(14)–2.0400(16) Å, respectively) as well as the C–Al–C and N–Al–N bond angles (113.08(13)–114.7(3)° and 87.0(2)–87.21(6)°, respectively) are in good agreement with those of **2aAlMe$_2$** and the related mononuclear congeners.[9a] The ^{1}H NMR spectrum of **2bAlMe$_2$** recorded in $CDCl_3$ contains two sets of four and two partially overlapping singlets that were assigned to the respective Al(CH_3) and N(CH_3) groups and indicate a mixture of the *meso*- and *R*,*R*/*S*,*S*-diastereomers. In case of **2dAlMe$_2$**, the unsymmetrical substitution pattern at aluminium gives rises to two singlets accounting for the two Al(CH_3) groups and the N(CH_3) groups appear as one singlet. Notably, the longer propylene-bridge in case of **2dAlMe$_2$** might causes the equivalence of the proton resonances of the *meso*- and *R*,*R*/*S*,*S*-diastereomers. In both complexes, free rotation about the N–C_{aryl} bond is evidenced by a simples set of resonances of the DMP group, *i.e.*, one singlet, one doublet, and one triplet integrating for 12, 4 and 2 protons, respectively.

4.3 Conclusion

In summary, we report about the synthesis of two general types of bis(amidoamine) ligands, in which the tertiary amine functions reside either on the lateral (type **2**) or terminal (type **1**) positions. Five synthetic procedures starting from readily available precursors have been employed and allowed for the gram-scale synthesis of the protio-ligands with yields ranging from 21 to 99%. Starting from the protio-ligands of type **1**, we could successfully isolate and fully characterize six complexes. Due to the flexibility of bridging groups, the reactions incorporating $Mg(HMDS)_2$ or $ZnEt_2$ afforded the mononuclear homoleptic complexes **1nMg** and **1nZn**, respectively, in-line with a Schlenk equilibrium. In contrast, originating from $AlH_3{\cdot}NMe_3$ and $Sn(HMDS)_2$ gave rise to the dinuclear complexes **1jAlH$_2$**, **1kAlH$_2$**, **1mSnHMDS**, and **1nSnHMDS**. The presence of reactive amide and hydride functions in the dinuclear complexes indicates possible applications, *i.e.*, as ligands for (transition) metals or as catalysts in their own rights. Using the piperazine-bridged ligand **2a**, dinuclear Janus-type complexes of aluminium and zinc could be obtained. The flexible ethylene-bridged ligand **2b** shows a variety of coordination modes upon complexation and the pro-chirality of the lateral tertiary amine groups affects the overall geometry of the obtained products. Mononuclear complexes of aluminium, magnesium, and tin were isolated after the reaction with $AlH_3{\cdot}NMe_3$, $Mg(HMDS)_2$, and $ZnEt_2$, respectively, while dinuclear complexes were derived from **2b** and trimethyl aluminium. The related species crystallize in centrosymmetric space groups and different diastereomers were identified from their molecular solid-state structures. The *R*,*R* or *S*,*S* form was observed in case of **2bMg**, **2bZn**, **2dAlMe$_2$**, while the *meso* form was observed for **2bAlH** and **2bAlMe$_2$**. In solution, however, a second set of resonances in the ^{1}H NMR spectrum indicates a mixture of the *meso* and the *R*,*R*/*S*,*S*-diastereomers for **2bAlMe$_2$**, while the spectra of **2bAlH**, **2bMg**, **2bZn**, and **2dAlMe$_2$** shown only one set of resonances. The catalytic activity of the heteroleptic complexes and their coordination capabilities towards transition metals will be further investigated in the future.

4.4 References

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4.5 Supporting information

General

All inorganic preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line or glovebox techniques (Mb 200G). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally through P_4O_{10}. Dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS- 800). D_6-Benzene and toluene were used as p.a. grade and were distilled from Na/benzophenone prior to use. $CDCl_3$ was dried by distillation from calcium hydride.

2-chloro-N-methylethan-1-amine hydrochloride, 2-chloroacetyl chloride, 2,2´-ethylenedianiline, trimethylamine, diisobutylamine, diethyl oxalate, dimethyl succinate, 2,6-dimethylaniline, 2,6-diisopropylaniline, isophthalaldehyde, N,N-diethylethylendiamine, N,N-diisopropylethylendiamine, diethylamine, piperidine, lithium aluminium hydride, sodium borohydride, 1,2-dibromoethane, 1,3-dibromopropane, potassium carbonate, m-xylylene dichloride, $Zn(Et)_2$ (1.0 M in hexanes), $AlMe_3$ (2.0 M in toluene) and $Sn(HMDS)_2$ were purchased from Sigma- Aldrich, whereas $Mg(HMDS)_2$[1] and $AlH_3{\cdot}NMe_3$[2] were prepared according to literature known procedures.

Characterization. The NMR spectra were recorded with a Bruker Avance 300 and 400 spectrometers (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CDCl_3$: δ(^1H) = 7.26), (C_6D_6: δ(^1H) = 7.16)or (THF-d_8: δ(^1H) = 1.72 and 3.58) and the solvent peak ($CDCl_3$: δ(^{13}C) = 77.16), (C_6D_6: δ(^{13}C) = 128.06) or (THF-d_8: δ(^{13}C) = 67.2 and 25.3), respectively. Mass spectrometric data were measured with a Waters LCT Micromass spectrometer. 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.

Protio ligand synthesis

Synthesis of 2-chloro-N-methylethan-1-amine hydrochloride:

2-chloro-N-methylethan-1-amine hydrochloride was prepared according to the literature procedure of Hirokawa *et al.*[3].

Synthesis of N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine:

2-chloro-N-methylethan-1-amine hydrochloride (2.60 g, 20.0 mmol) and 2,6-dimethylaniline (7.40 mL, 60.0 mmol) were mixed in a closed reaction vessel and heated to 130 °C overnight before water (120 mL), EtOAc (20 mL) and an aqueous solution of NaOH (2M, 10 mL) were added to the reaction mixture. The organic phase was separated, the solvent was removed in vacuum and the resulting residue was dissolved in pentane (100 mL) followed by addition of acetic acid (4 mL) and water (50 mL). The phases were again separated, whereas the aqueous phase was further treated with NaOH (10 g), stirred and extracted with Et_2O. Afterwards, the combined organic layers were dried over $MgSO_4$ followed by solvent removal to obtain 2.16 g (76 %) of N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine as an orange viscous liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 6.99 (d, J=7.4 Hz, 2H, arom. meta H), 6.81 (t, J=7.4 Hz, 1H, arom. para H), 3.08 (t, J=5.7 Hz, 2H, $NHC\mathit{H}_2CH_2NHCH_3$), 2.80 (t, J= 5.7 Hz, 2H, $NHCH_2C\mathit{H}_2NHCH_3$), 2.48 (s, 3H, $NC\mathit{H}_3$), 2.31 (s, 6H, $PhC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.5 (*i*-C_6H_3), 129.5 (*o*-C_6H_3), 128.9 (*m*-C_6H_3), 121.8 (*p*-C_6H_3), 52.2 ($NHCH_2\mathit{C}H_2NHCH_3$), 47.8 ($NH\mathit{C}H_2CH_2NHCH_3$), 36.4 ($N\mathit{C}H_3$), 18.7 ($Ph\mathit{C}H_3$). HRMS (Methode) [m/z]: 179.156 (ES+)

Synthesis of 2,2'-(piperazine-1,4-diyl)bis(N-(2,6-dimethylphenyl)acetamide):

2,2'-(piperazine-1,4-diyl)bis(N-(2,6-dimethylphenyl)acetamide) was prepared according to the literature procedure of Aalla *et al.*[4].

Synthesis of N^1-(2,6-diisopropylphenyl)-N^2-methylethane-1,2-diamine:

2-chloro-N-methylethan-1-amine hydrochloride (2.60 g, 20.0 mmol) and 2,6-diisopropylaniline (10.6 g, 60.0 mmol) were mixed in a closed reaction vessel and heated to 130 °C overnight before EtOAc (100 mL) and an aqueous solution of NaOH (2M, 100 mL) were added to the reaction mixture. The organic phase was separated, the solvent was removed in vacuum and the resulting residue was dissolved in pentane (100 mL) followed by addition of acetic acid (5 mL) and water (100 mL). The phases were again separated, whereas the aqueous phase was further treated with NaOH (10 g), stirred and extracted with EtOAc (50 mL). Afterwards, the combined organic layers were dried over Na_2SO_4 followed by solvent removal to obtain 3.01 g (64 %) of N^1-(2,6-diisopropylphenyl)-N^2-methylethane-1,2-diamine as a red liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 7.28-7.19 (m, 3H, arom. H), 3.51 (sept, J= 6.8Hz, 2H, $CH(CH_3)_2$), 3.15 (t, J= 6.0 Hz, 2H, $CH_3NHCH_2CH_2$), 2.99 (t, J= 6.0 Hz, 2H, $CH_3NHCH_2CH_2$), 2.65 (s, 3H, NCH_3), 1.42 (d, J=6.8Hz, 12H, $CH(CH_3)_2$. $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 143.4 (*i*-C_6H_3), 142.4 (*o*-C_6H_3), 123.6 (*m*-C_6H_3), 123.4 (*p*-C_6H_3), 52.2 ($CH_3NHCH_2CH_2$), 51.0 ($CH_3NHCH_2CH_2$), 36.4 (NCH_3), 27.5 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$). HRMS (Methode) [m/z]: 235.218 (ES+)

Synthesis of Bis[diethylaminoethyl]-N,N'-m-xylylendiimine:

Isophthalaldehyde (2.01 g, 15.0 mmol) was added to a stirred solution of N,N-diethylethylendiamine (3.50 g, 30.0 mmol) in EtOH (15 mL) and the solution was stirred overnight. Solvent removal and drying of the product under vacuum gives 4.95 g (99 %) of bis[diethylaminoethyl]-N,N'-m-xylylendiimine as an yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 8.26 (s, 2H, C*H*PhC*H*), 7.96 (s, 1H, 1), 7.73 (d, J=7.7 Hz, 2H, *3*), 7.37 (t, J=7.7 Hz, 1H, *4*), 3.66 (t, J=7.1 Hz, 4H, NCH_2CH_2), 2.72 (t, J=7.1 Hz, 4H, NCH_2CH_2), 2.54 (q, J=7.3 Hz, 8H, NCH_2CH_3), 0.98 (t, J=7.3 Hz, 12H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 161.2 (*C*HPh*C*H), 136.7 (2), 129.7 (3), 128.8 (4), 128.0 (1), 59.8

($NCH_2\mathit{C}H_2$), 53.4 ($N\mathit{C}H_2CH_2$), 47.5 ($N\mathit{C}H_2CH_3$), 11.9 ($NCH_2\mathit{C}H_3$). HRMS (Methode) [m/z]: 331.286 (ES+)

Synthesis of Bis[diisopropylaminoethyl]-N,N'-m-xylylendiimine:

Isophthalaldehyde (2.01 g, 15.0 mmol) was added to a stirred solution of N,N-diisopropylethylendiamine (4.33 g, 30.0 mmol) in EtOH (15 mL) and the solution was stirred overnight. Solvent removal and drying of the product under vacuum gives 5.80 g (99 %) of bis[diisopropylaminoethyl]-N,N'-m-xylylendiimine as an yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 8.24 (s, 2H,C*H*PhC*H*), 7.99 (t, J=1.6 Hz, 2H, *1*), 7.76 (dd, J=1.6 Hz, J=7.6 Hz, 2H, *3*), 7.41 (t, J=7.6 Hz, 1H, *4*), 3.60 (t, J=7.2 Hz, 4H, $NHC\mathit{H}_2CH_2$), 2.99 (sept, J= 6.62, 4H, $CH(CH_3)_2$), 2.70 (t, J=7.2 Hz, 4H, $NHCH_2C\mathit{H}_2$), 0.98 (d, J=6.62 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 161.0 (*C*HPh*C*H), 136.8 (2), 129.7 (3), 128.9 (4), 128.1 (1), 63.5 ($NHCH_2\mathit{C}H_2$), 49.0 ($\mathit{C}H(CH_3)_2$),46.2 ($NH\mathit{C}H_2CH_2$), 30.0 ($CH(\mathit{C}H_3)_2$). HRMS (Methode) [m/z]: 387.348 (ES+)

Synthesis of N,N'-(1,3-phenylene)bis(2-chloroacetamide):

N,N'-(1,3-phenylene)bis(2-chloroacetamide) was prepared according to the literature procedure of Fyles *et al.*[5].

Synthesis of N,N'-(1,3-phenylene)bis(2-(diethylamino)acetamide):

Diethylamine (14.0 g, 200 mmol) was added to a stirred solution of N,N'-(1,3-phenylene)bis(2-chloroacetamide) (13.0 g, 50.0 mmol) in EtOH (120 mL) and heated to 80 °C for 15 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (75 mL) as well as water (50 mL). The aqueous solution was extracted with $CHCl_3$ (3x50 mL), dried over $MgSO_4$ followed by solvent removal to obtain 15.0 g (89 %) of N,N'-(1,3-phenylene)bis(2-(diethylamino)acetamide).

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 9.43 (s, 2H, NH), 7.85 (t, J = 2.0 Hz, 1H, 1), 7.40-7.36 (m, 2H, 3), 7.30-7.25 (m, 1H, 4), 3.14 (s, 4H, C*H*$_2$CO), 2.65 (q, J = 7.21 Hz, 8H, C*H*$_2$CH$_3$), 1.08 (t, J = 7.21 Hz, 12H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 170.5 (*C*O), 138.4 (2), 129.7 (4), 115.0 (3), 110.1 (1) , 58.0 (CO*C*H$_2$), 49.0 (*C*H$_2$CH$_3$), 12.4 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 335.24 (ES+).

Synthesis of N,N'-(1,3-phenylene)bis(2-(piperidin-1-yl)acetamide):

Piperidine (7.80 g, 92.0 mmol) was added to a stirred solution of N,N'-(1,3-phenylene)bis(2-chloroacetamide) (6.00 g, 23.0 mmol) in EtOH (60 mL) and heated to 80 °C for 24 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (30 mL). The aqueous solution was extracted with $CHCl_3$ (3x25 mL), dried over $MgSO_4$ followed by solvent removal to obtain 6.30 g (76 %) of N,N'-(1,3-phenylene)bis(2-(piperidin-1-yl)acetamide) as a brown solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 9.26 (s, 2H, NH), 7.84 (t, J = 2.0 Hz, 1H, 4-C*H*$_{arom}$), 7.38-7.34 (m, 2H, 3-C*H*$_{arom}$), 7.30-7.24 (m, 1H, 1-C*H*$_{arom}$), 3.05 (s, 4H, COC*H*$_2$), 2.52 (m, 8H, α-pip), 1.63 (m, 8H, β-pip), 1.50-1.45 (m, 4H, γ-pip). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 169.3 (*C*O), 138.4 (2-C*H*$_{arom}$), 129.7 (4-C*H*$_{arom}$), 115.2 (3-*C*H$_{arom}$), 110.4 (1-C*H*$_{arom}$), 63.0 (CO*C*H$_2$), 55.0 (α-pip), 26.3 (β-pip), 23.7 (γ-pip).

Synthesis of N,N'-(1,2-phenylene)bis(2-chloroacetamide):

N,N'-(1,2-phenylene)bis(2-chloroacetamide) was prepared according to the literature procedure of Beer *et al.*[6].

Synthesis of N,N'-(1,2-phenylene)bis(2-(diethylamino)acetamide):

N,N'-(1,2-phenylene)bis(2-(diethylamino)acetamide) was prepared according to the literature procedure of Singh *et al.*[7].

Synthesis of N,N'-(1,2-phenylene)bis(2-(piperidin-1-yl)acetamide):

Piperidine (8.50 g, 100 mmol) was added to a stirred solution of N,N'-(1,2-phenylene)bis(2-chloroacetamide) (6.50 g, 25.0 mmol) in EtOH (60 mL) and heated to 80 °C for 15 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (38 mL) as well as water (25 mL). The aqueous solution was extracted with $CHCl_3$ (3x25 mL) and dried over $MgSO_4$. After solvent removal the crude product was recrystallized from EtOH to obtain 4.80 g (54 %) of N,N'-(1,2-phenylene)bis(2-(piperidin-1-yl)acetamide) as white needles.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 9.30 (s, 2H, N*H*), 7.60-7.56 (m, 2H, ortho-*H*), 7.21-7.17 (m, 2H, meta-*H*), 3.12 (s, 4H, CH_2CO), 2.53 (t, J = 5.0 Hz, 8H, α-pip), 1.67-1.59 (m, 8H, β-pip), 1.49-1.46 (m, 4H, γ-pip). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 169.9 (*C*O), 130.2 (ipso-*C*), 126.2 (meta-*C*), 124.9 (ortho-*C*), 62.8 (*C*H_2CO), 55.2 (α-pip), 26.2 (β-pip), 23.7 (γ-pip). HRMS (Methode) [m/z]: 359.2 (ES+)

Synthesis of N,N'-(pyridine-2,6-diyl)bis(2-chloroacetamide):

N,N'-(pyridine-2,6-diyl)bis(2-chloroacetamide) was prepared according to the literature procedure of Wang *et al.*[8].

Synthesis of N,N'-(pyridine-2,6-diyl)bis(2-(diethylamino)acetamide):

Diethylamine (8.70 g, 120 mmol) was added to a stirred solution of N,N'-(pyridine-2,6-diyl)bis(2-chloroacetamide) (7.40 g, 28.0 mmol) in EtOH (90 mL) and heated to 80 °C for 24 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (45 mL) as well as water (25 mL). The aqueous solution was extracted with $CHCl_3$ (3x30 mL), dried over $MgSO_4$ followed by solvent removal to obtain 9.30 g (99 %) of N,N'-(pyridine-2,6-diyl)bis(2-(diethylamino)acetamide) as a black solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 9.56 (br, 2H, N*H*), 7.91 (d, J = 7.8 Hz, 2H, meta *H*), 7.65 (t, J = 7.8 Hz, 1H, para *H*), 3.12 (s, 4H, COCH_2), 2.62 (q, J = 7.2 Hz, 8H, CH_2CH$_3$), 1.06 (t, J = 7.2 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 170.9 (*C*O), 149.4 (ortho *C*), 140.4 (para *C*), 109.2 (meta *C*), 58.1 (CO*C*H$_2$), 48.8 (*C*H$_2$CH$_3$), 12.3 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 336.2 (ES+).

Synthesis of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-chloroacetamide):

2-chloroacetyl chloride (7.30 g, 65.0 mmol) was added to a stirred solution of 2,2´-ethylenedianiline (5.80 g, 26.0 mmol) and triethylamine (7.80 g, 78.0 mmol) in THF (150 mL) at 0 °C. The solution was allowed to warm to room temperature and was further stirred for 15 hours resulting in a grey precipitate. The precipitate was filtered off, washed with water, THF and again water to obtain 8.20 g (86 %) of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-chloroacetamide).

^{1}H NMR (300 MHz, DMSO-d_6): *δ(ppm)* = 9.78 (s, 2H, N*H*), 7.38 (dd, J = 7.4 Hz, J = 1.5, 2H, arom *H*), 7.28 – 7.14 (m, 6H, arom *H*), 4.34 (s, 4H, COCH_2), 2.79 (s, 4H, CH_2CH_2). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): *δ (ppm)* = 165.4 (CO), 136.0 (arom. C), 135.1 (arom. C), 129.7 (arom. C), 126.4 (arom. C), 126.1 (arom. C), 126.1 (arom. C), 43.2 (CH$_2$Cl), 31.3 (CH$_2$CH$_2$). HRMS (Methode) [m/z]: 365.1 (ES+).

Synthesis of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diethylamino)acetamide):

Diethylamine (3.20 g, 44.0 mmol) was added to a stirred solution of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-chloroacetamide) (4.00 g, 11.0 mmol) in EtOH (33 mL) and heated to 80 °C for 24 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (17 mL) as well as water (11 mL). The aqueous solution was extracted with $CHCl_3$ (3x11 mL), dried over $MgSO_4$ followed by solvent removal to obtain 4.70 g (97 %) of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diethylamino)acetamide) as a black solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 9.50 (br, 2H, N*H*), 8.07 (d, J = 7.8 Hz, 2H, C$H_{arom.}$), 7.28-7.22 (m, 2H, C$H_{arom.}$), 7.12-7.03 (m, 4H, CH_{arom}), 3.20 (s, 4H, COCH_2), 2.89 (s, 4H, CH_2CH_2), 2.65 (q, J = 6.9 Hz, 8H, CH_2CH$_3$), 1.04 (t, J = 7.2 Hz, 12H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 170.1 (*C*O), 135.4 (arom. *C*), 130.9 (arom. *C*), 129.3 (arom. *C*), 127.5 (arom. *C*), 124.8 (arom. *C*), 122.3 (arom. *C*), 58.2 (CO*C*H$_2$), 48.8 (*C*H$_2$CH$_3$), 31.7 (*C*H$_2$*C*H$_2$), 12.4 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 439.3 (ES+)

Synthesis of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diisobutylamino)acetamide):

Diisobutylamine (3.35 g, 26.0 mmol) was added to a stirred solution of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-chloroacetamide) (2.40 g, 6.50 mmol) in DMSO (10 mL) and heated to 70 °C for three days. The mixture was allowed to cool to room temperature followed by addition of water (100 mL). The aqueous solution was extracted with DCM (100 mL), followed by washing of the organic phase with brine (50 mL). Drying over $MgSO_4$ and solvent removal gave 3.20 g (90 %) of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diisobutylamino)acetamide).

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 8.99 (br, 2H, NH), 7.85 (d, J = 7.4 Hz, 2H, *1*), 7.26-7.19 (m, 2H, *2*), 7.08-7.07 (m, 4H, *3+4*), 3.16 (s, 4H, COCH_2), 2.90 (s, 4H, CH_2CH_2), 2.22 (d, J = 7.5 Hz, 8H, CH_2CH(CH$_3$)$_2$), 1.76 (nonett, 4H, CH$_2$CH(CH$_3$)$_2$), 0.84 (d, J = 6.5 Hz, 24H, CH$_2$CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 170.3 (*C*O), 135.1 (arom. *C*), 132.5 (arom. *C*), 129.0 (arom. *C*), 127.2 (arom. *C*), 125.4 (arom. *C*), 123.7 (arom. *C*), 64.3 (*C*H$_2$C(CH$_3$)$_2$), 60.8 (CO*C*H$_2$), 30.7(*C*H$_2$*C*H$_2$), 26.3 (CH$_2$*C*(CH$_3$)$_2$), 21.1 (CH$_2$C(*C*H$_3$)$_2$). HRMS (Methode) [m/z]: 551.4 (ES+)

Synthesis of N,N'-(oxybis(2,1-phenylene))bis(2-chloroacetamide):

N,N'-(oxybis(2,1-phenylene))bis(2-chloroacetamide) was prepared according to the literature procedure of Kocina *et al.*[9].

Synthesis of N,N'-(oxybis(2,1-phenylene))bis(2-(diethylamino)acetamide):

Diethylamine (3.00 g, 40.0 mmol) was added to a stirred solution of N,N'-(oxybis(2,1-phenylene))bis(2-chloroacetamide) (3.50 g, 10.0 mmol) in EtOH (30 mL) and heated to 80 °C for 15 hours. The mixture was allowed to cool to room temperature followed by solvent removal and addition of saturated $NaHCO_3$ solution (20 mL) as well as water (10 mL). The aqueous solution was extracted with DCM (2x15 mL), dried over $MgSO_4$ followed by solvent removal to obtain 3.70 g (86 %) of N,N'-(oxybis(2,1-phenylene))bis(2-(diethylamino)acetamide).

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 10.0 (br, 2H, N*H*), 8.51 (dd, J = 1,6 Hz, J = 8.2 Hz, 2H, *4*), 7.15 (dt, J = 1.3 Hz, J = 8.0 Hz, 2H, *2*), 7.01 (dt, J = 1.5 Hz, J = 8.2 Hz, 2H, *3*), 6.75 (dd, J = 1.8 Hz, J = 8.0 Hz, *1*), 3.12 (s, 4H, COCH_2), 2.49 (q, J = 7.2 Hz, 8H, CH_2CH$_3$), 0.90 (t, J = 7.2 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 170.5 (CO), 145.3 (arom. *C*), 129.7 (arom. *C*), 124.8 (arom. *C*), 124.4 (arom. *C*), 120.8 (arom. *C*), 117.7 (arom. *C*), 58.4 (*C*H$_2$CH$_3$), 48.6 (CO*C*H$_2$), 12.4 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 427.3 (ES+)

Synthesis of N^1,N^2-bis(2-(dimethylamino)ethyl)oxalamide:

N^1,N^2-bis(2-(dimethylamino)ethyl)oxalamide was prepared according to the literature procedure of Real *et al.*[10].

Synthesis of N^1,N^2-bis(2-(diethylamino)ethyl)oxalamide:

N,N-diethylethylenediamine (5.80 g, 50.0 mmol) and diethyl oxalate (2.90 g, 20.0 mmol) were mixed and stirred at 130 °C overnight. After drying at vacuum 5.60 g (98 %) of N^1,N^2-bis(2-(diethylamino)ethyl)oxalamide could be isolated as a pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 7.86 (br, 2H, NH), 3.33 (q, J = 6.0 Hz, 4H, NHCH_2CH$_2$), 2.57 (t, J = 6.0Hz, 4H, NHCH$_2$CH_2), 2.53 (q, J = 7.2 Hz, 8H, CH_2CH$_3$), 1.00 (t, J = 7.2 Hz, 12H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 159.9 (CO), 51.3 (NHCH$_2$*C*H$_2$), 47.0 (*C*H$_2$CH$_3$), 37.4 (NH*C*H$_2$CH$_2$), 12.0 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 287.2 (ES+)

Synthesis of N^1,N^2-bis(2-(diisopropylamino)ethyl)oxalamide:

N,N-diisopropylethylenediamine (3.17 g, 22.0 mmol) and diethyl oxalate (1.46 g, 10.0 mmol) were mixed and stirred at 120 °C overnight. After drying at vacuum 3.40 g (99 %) of N^1,N^2-bis(2-(diisopropylamino)ethyl)oxalamide could be isolated as a pale yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 7.92 (br, 2H, NH), 3.27 (q, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 3.01 (sept, J = 6.4 Hz, 4H, $CH(CH_3)_2$), 2.62 (t, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 1.01 (d, J = 6.4 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 159.9 (CO), 48.1 ($NHCH_2CH_2$), 43.1 ($NHCH_2CH_2$), 38.7 ($CH(CH_3)_2$), 20.9 ($CH(CH_3)_2$). HRMS (Methode) [m/z]: 343.3 (ES+)

Synthesis of N^1,N^2-bis(2-(diisobutylamino)ethyl)oxalamide:

N,N-diisobutylethylenediamine (1.89 g, 11.0 mmol) and diethyl oxalate (730 mg, 5.00 mmol) were mixed and stirred at 120 °C overnight. After drying at vacuum 1.98 g (99 %) of N^1,N^2-bis(2-(diisobutylamino)ethyl)oxalamide could be isolated as a redish solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 7.89 (br, 2H, NH), 3.32 (q, J = 5.8 Hz, 4H, $NHCH_2CH_2$), 2.49 (t, J = 5.8 Hz, 4H, $NHCH_2CH_2$), 2.09 (d, J = 7.3 Hz, 8H, $CH_2CH(CH_3)_2$), 1.69 (nonett, J = 6.6 Hz, 4H, $CH_2CH(CH_3)_2$), 0.89 (d, J = 6.6 Hz, 24 Hz, $CH_2CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 159.8 (CO), 63.9 ($CH_2CH(CH_3)_2$), 53.6 ($NHCH_2CH_2$), 37.3 ($NHCH_2CH_2$), 26.7 ($CH_2CH(CH_3)_2$), 21.0 ($CH_2CH(CH_3)_2$). HRMS (Methode) [m/z]: 399.4 (ES+)

Synthesis of N^1,N^4-bis(2-(diethylamino)ethyl)succinamide:

N,N-diethylethylenediamine (5.80 g, 50.0 mmol) and dimethyl succinate (2.92 g, 20.0 mmol) were mixed and stirred at 120 °C overnight. After drying at vacuum 6.20 g (99 %) of N^1,N^4-bis(2-(diethylamino)ethyl)succinamide could be isolated as an orange solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = 6.44 (br, 2H, NH), 3.27 (q, J = 5.7 Hz, 4H, $NHCH_2$), 2.52 (m, 16H, $CH_2N(CH_2CH_3)_2$ + CH_2CH_2), 1.00 (t, J = 7.1 Hz, 12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 172.1 (CO), 51.5 ($NHCH_2CH_2$) , 46.8 (CH_2CH_3), 37.1 ($NHCH_2CH_2$), 31.9 (CH_2CH_2), 11.8 (CH_2CH_3). HRMS (Methode) [m/z]: 315.3 (ES+)

Synthesis of L(Et-Me$_2$)H$_2$ (1a):

Lithium aluminium hydride (760 mg, 20.0 mmol) was added slowly to a stirred solution of N^1,N^2-bis(2-(dimethylamino)ethyl)oxalamide (1.84 g, 8.00 mmol) in dry THF (80 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C for three days, cooled down to room temperature and water (3 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 910 mg (56 %) of L(Et-Me$_2$)H$_2$ (**1a**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 2.74 (s, 4H, C*H*$_2$C*H*$_2$), 2.68 (t, J = 6.2 Hz, 4H, NHC*H*$_2$CH$_2$), 2.40 (t, J = 6.2 Hz, 4H, NHCH$_2$C*H*$_2$), 2.20 (s, 12H, N(C*H*$_3$)$_2$), 2.12 (br, 2H, N*H*CH$_2$CH$_2$).^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 59.2 (NHCH$_2$*C*H$_2$), 49.6 (*C*H$_2$*C*H$_2$), 47.4 (NH*C*H$_2$CH$_2$), 45.7 (N(*C*H$_3$)$_2$). HRMS (Methode) [m/z]: 203.2 (ES+)

Synthesis of L(Et-Et$_2$)H$_2$ (1b):

Lithium aluminium hydride (380 mg, 10.0 mmol) was added slowly to a stirred solution of N^1,N^2-bis(2-(diethylamino)ethyl)oxalamide (1.15 g, 4.00 mmol) in dry THF (40 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C for three days, cooled down to room temperature and water (1 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 410 mg (41 %) of L(Et-Et$_2$)H$_2$ (**1b**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 2.74 (d, J = 0.8 Hz, 4H, C*H*$_2$C*H*$_2$), 2.67 (t, J = 6.3 Hz, 4H, NHC*H*$_2$CH$_2$), 2.56-2.47 (m, 12H, C*H*$_2$N(C*H*$_2$CH$_3$)$_2$), 1.98 (br, 2H, NH), 0.99 (t, J = 7.1 Hz, 12H, CH$_2$N(CH$_2$C*H*$_3$)$_2$).^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 52.8 (*C*H$_2$N(CH$_2$CH$_3$)$_2$), 49.7(NH*C*H$_2$CH$_2$), 47.7 (*C*H$_2$*C*H$_2$) , 47.2 (CH$_2$N(*C*H$_2$CH$_3$)$_2$), 11.9 (CH$_2$N(CH$_2$*C*H$_3$)$_2$). HRMS (Methode) [m/z]: 259.3 (ES+)

Synthesis of L(Et-^{i}Pr$_2$)H$_2$ (1c):

Lithium aluminium hydride (760 mg, 20.0 mmol) was added slowly to a stirred solution of N^1,N^2-bis(2-(diisopropylamino)ethyl)oxalamide (2.74 g, 8.00 mmol) in dry THF (80 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C for three days, cooled down to room temperature and water (5 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 2.20 g (87 %) of L(Et-^{i}Pr$_2$)H$_2$ (**1c**).

^{1}H NMR (400 MHz, CDCl$_3$): *δ(ppm)* = 2.91 (sept, J = 5.6 Hz, 4H, C*H*(CH$_3$)$_2$), 2.65 (s, 4H, CH2CH2), 2.53-2.46 (m, 8H, NHC*H*$_2$C*H*$_2$), 0.92 (d, J = 6.6 Hz, 24H, CH(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz,CDCl$_3$): *δ (ppm)* = 49.8 (NHCH$_2$*C*H$_2$), 49.7(NH*C*H$_2$CH$_2$), 48.1 (*C*H$_2$*C*H$_2$), 44.5 (C*H*(CH$_3$)$_2$), 20.8 (CH(C*H*$_3$)$_2$). HRMS (Methode) [m/z]: 315.3 (ES+)

Synthesis of L(Et-^{i}Bu$_2$)H$_2$ (1d):

Lithium aluminium hydride (380 mg, 10.0 mmol) was added slowly to a stirred solution of N^1,N^2-bis(2-(diisobutylamino)ethyl)oxalamide (1.60 g, 4.00 mmol) in dry THF (80 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C for three days, cooled down to room temperature and water (3 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 1.10 g (74 %) of L(Et-^{i}Bu$_2$)H$_2$ (**1d**).

^{1}H NMR (400 MHz, CDCl$_3$): *δ(ppm)* = 2.75 (s, 4H, C*H*$_2$C*H*$_2$), 2.63 (t, J = 5.7 Hz, 4H, NHC*H*$_2$CH$_2$), 2.46 (t, J = 5.7 Hz, 4H, NHCH$_2$C*H*$_2$), 2.06 (d, J = 7.2 Hz, 8H, C*H*$_2$CH(CH$_3$)$_2$), 1.69 (nonett, J = 6.9 Hz, 4H, CH$_2$C*H*(CH$_3$)$_2$), 0.86 (d, J = 6.7 Hz, 24H, CH$_2$CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (101 MHz,CDCl$_3$): *δ (ppm)* = 64.4 (*C*H$_2$CH(CH$_3$)$_2$), 54.8 (NHCH$_2$*C*H$_2$), 49.5 (NH*C*H$_2$CH$_2$), 47.7 (*C*H$_2$*C*H$_2$), 26.6 (CH$_2$*C*H(CH$_3$)$_2$), 21.1 (CH$_2$CH(*C*H$_3$)$_2$). HRMS (Methode) [m/z]: 371.4 (ES+)

Synthesis of L(Bu-Et$_2$)H$_2$ (1e):

Lithium aluminium hydride (380 mg, 10.0 mmol) was added slowly to a stirred solution of N^1,N^4-bis(2-(diethylamino)ethyl)succinamide (1.26 g, 4.00 mmol) in dry THF (40 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C for three days, cooled down to room temperature and water (1 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 520 mg (45 %) of L(Bu-Et$_2$)H$_2$ (**1e**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 2.67-2.62 (m, 8H), 2.55-2.44 (m, 12H), 2.01 (br, 2H, NH), 1.55-1.53 (m, 4H, $CH_2CH_2CH_2CH_2$), 0.99 (t, J = 7.1 Hz, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 52.7 ($CH_2N(CH_2CH_3)_2$), 50.1 ($NHCH_2CH_2$), 47.7 (CH_2CH_2 CH_2CH_2), 47.3 ($CH_2N(CH_2CH_3)_2$), 28.1 (CH_2CH_2 CH_2CH_2), 12.0 ($CH_2N(CH_2CH_3)_2$). HRMS (Methode) [m/z]: 287.3 (ES+)

Synthesis of L(Xyl-Et$_2$)H$_2$ (1f):

Sodium borohydride (1.70 g, 45.0 mmol) was added portion wise to a solution of bis[diethylaminoethyl]-N,N'-m-xylylendiimine (4.95 g, 45.0 mmol) in EtOH (30 mL) at 0 °C followed by stirring of the reaction at 50 °C for three days. After the mixture was cooled to room temperature, water (10 mL) was added and the mixture was further stirred for 20 minutes before the majority of the solvent was removed in vacuum. The remaining solution was mixed with Et_2O (20 mL) and water (10 mL) and the aqueous phase was extracted with Et_2O (2x20 mL). The combined organic layers were dried over Na_2SO_4 followed by solvent removal to obtain 4.40 g (88 %) of L(Xyl-Et$_2$)H$_2$ (**1f**) as an yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.18-7.10 (m, 4H, C_6H_4), 3.70 (s, 4H, CH_2PhCH_2), 2.59 (t, J=6.0 Hz, 4H, $NHCH_2CH_2$), 2.47 (t, J=6.0 Hz, 4H, $NHCH_2CH_2$), 2.40 (q, J=7.1 Hz, 8H, NCH_2CH_3), 2.05 (br, 2H, NH), 0.91 (t, J=7.1 Hz, 12H, NCH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 140.5 (2), 128.2 (1), 127.8 (4), 126.5 (3), 53.9 ($NHCH_2CH_2$), 52.5 (CH_2PhCH_2), 46.9 (NCH_2CH_3), 46.8 ($NHCH_2CH_2$), 11.7 (NCH_2CH_3). HRMS (Methode) [m/z]: 335.317 (ES+)

Synthesis of L(Xyl-^{i}Pr$_2$)H$_2$ (1g):

Sodium borohydride (1.70 g, 45.0 mmol) was added portion wise to a solution of bis[diisopropylaminoethyl]-N,N'-m-xylylendiimine (5.80 g, 15.0 mmol) in MeOH (50 mL) at room temperature followed by refluxing overnight. Afterwards, saturated NH_4Cl (aq.) (20 mL) solution and Et_2O (20 mL) were added to the mixture followed by extraction of the aqueous phase with Et_2O (2x20 mL). The combined organic layers were dried over $MgSO_4$ followed by solvent removal to obtain 4.26 g (73 %) of L(Xyl-^{i}Pr$_2$)H$_2$ (**1g**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.24-7.15 (m, 4H, C_6H_4), 3.76 (s, 4H, CH_2PhCH_2), 2.94 (sept., J=6.6 Hz, 4H, $CH(CH_3)_2$), 2.57 (br, 8H, $NHCH_2CH_2$), 1.90 (br, 2H, NH), 0.96 (d, J=6.6 Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 140.8 (2), 128.4 (1), 127.8 (4), 126.5 (3), 54.1 (CH_2PhCH_2), 48.8 ($NHCH_2CH_2$), 48.0 ($NCH(CH_3)_2$), 44.3 ($NHCH_2CH_2$), 21.9 ($NCH(CH_3)_2$). HRMS (Methode) [m/z]: 391.380 (ES+)

Synthesis of L(o-Ph-Et$_2$)H$_2$ (1h):

Lithium aluminium hydride (4.70 g, 119 mmol) was added slowly to a stirred solution of N,N'-(1,2-phenylene)bis(2-(diethylamino)acetamide) (10.6 g, 34.0 mmol) in dry THF (160 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (9 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 7.90 g (76 %) of L(o-Ph-Et$_2$)H$_2$ (**1h**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 6.80-6.61 (m, 4H, C_6H_4), 4.08 (br, 2H, NH), 3.12 (t, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 2.76 (t, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 2.56 (q, J = 7.2 Hz, 8H, CH_2CH_3), 1.04 (t, J = 7.2 Hz, 12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 137.6 (*i*-C_6H_4), 118.6 (*m*-C_6H_4), 110.9 (*o*-C_6H_4), 51.9 ($NHCH_2CH_2$), 46.8 (CH_2CH_3), 41.6 ($NHCH_2CH_2$), 12.0 (CH_2CH_3). HRMS (Methode) [m/z]: 307.29 (ES+)

Synthesis of L(o-Ph-Pip)H_2 (1i):

Lithium aluminium hydride (1.90 g, 46.9 mmol) was added slowly to a stirred solution of N,N'-(1,2-phenylene)bis(2-(piperidin-1-yl)acetamide) (4.80 g, 13.4 mmol) in dry THF (100 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (4 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 3.20 g (73 %) of L(o-Ph-Pip)H_2 (**1i**) as a pink solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 6.78-6.75 (m, 2H, *o*-C_6H_4), 6.66-6.62 (m, 2H, *m*-C_6H_4), 4.09 (br, 2H, NH), 3.16-3.15 (m, 4H, $NHCH_2CH_2$), 2.66 (t, J = 6.1 Hz, 4H, $NHCH_2CH_2$), 2.44 (br, 8H, α-pip), 1.63-1.55 (m, 8H, β-pip), 1.48-1.44 (m, 4H, γ-pip). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 137.5 (*i*-C_6H_4), 118.6 (*m*-C_6H_4), 111.0 (*o*-C_6H_4), 57.8 ($NHCH_2CH_2$), 54.6 (α-pip), 41.0 ($NHCH_2CH_2$), 26.2 (β-pip), 24.6 (γ-pip). HRMS (Methode) [m/z]: 331.3 (ES+)

Synthesis of L(m-Ph-Et_2)H_2 (1j):

Lithium aluminium hydride (6.40 g, 160 mmol) was added slowly to a stirred solution of N,N'-(1,3-phenylene)bis(2-(diethylamino)acetamide) (15.0 g, 45.0 mmol) in dry THF (200 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (13 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 9.80 g (72 %) of L(m-Ph-Et_2)H_2 (**1j**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 6.98 (t, J = 7.9 Hz, 1H, 4), 6.03 (dd, J = 2.2 Hz, J = 7.9 Hz, 2H, 3), 5.94 (t, J = 2.2 Hz, 1H, 1), 4.21 (br, 2H, NH), 3.11 (dt, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 2.67 (t, J = 5.9 Hz, 4H, $NHCH_2CH_2$), 2.55 (q, J = 7.1 Hz, 8H, CH_2CH_3), 1.02 (t, J = 7.1 Hz, 12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 150.0 (2), 129.9 (4), 103.1 (3), 97.7 (1), 51.8 ($NHCH_2CH_2$), 46.8 (CH_2CH_3), 41.5 ($NHCH_2CH_2$), 11.9 (CH_2CH_3). HRMS (Methode) [m/z]: 307.29 (ES+)

Synthesis of L(m-Ph-Pip)H_2 (1k):

Lithium aluminium hydride (1.00 g, 25.0 mmol) was added slowly to a stirred solution of N,N'-(1,3-phenylene)bis(2-(piperidin-1-yl)acetamide) (1.80 g, 5.00 mmol) in dry THF (50 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (2 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 930 mg (56 %) of L(m-Ph-Pip)H_2 (**1k**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 6.98 (t, J = 7.9Hz, 1H, 1), 6.03 (dd, J = 2.1 Hz, J = 7.9 Hz, 2H, 3), 5.94 (t, J = 2.1 Hz, 1H, 4), 4.24 (t, J = 5.3 Hz, 2H, NH), 3.14 (dt, J = 5.3 Hz, J = 6.0 Hz, 4H, NHC$H_2$$CH_2$), 2.56 (t, J = 6.0 Hz, 4H, NHC$H_2$$CH_2$), 2.39 (br, 8H, α-pip), 1.61-1.53 (m, 8H, β-pip), 1.47-1.43 (m, 4H,γ-pip). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 149.9 (2), 130.0 (4), 103.0 (3), 97.6 (1), 57.7 (NHC$H_2$$CH_2$), 54.5 (α-pip), 40.6 (NHC$H_2$$CH_2$), 26.1 (β-pip), 24.6 (γ-pip). HRMS (Methode) [m/z]: 331.29 (ES+)

Synthesis of L(o-Pyr-Et_2)H_2 (1l):

Lithium aluminium hydride (390 mg, 10.3 mmol) was added slowly to a stirred solution of N,N'-(pyridine-2,6-diyl)bis(2-(diethylamino)acetamide) (1.00 g, 3.00 mmol) in dry THF (30 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (3 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 580 mg (63 %) of L(o-Pyr-Et_2)H_2 (**1l**) as a dark yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.21 (t, J = 7.8 Hz, 1H, *p*-C_6H_3N), 5.71 (d, J = 7.8 Hz, 2H, *m*-C_6H_3N), 4.73 (br, 2H, N*H*), 3.24 (dt, J = 6.2 Hz, 4H, NHC$H_2$$CH_2$), 2.63 (t, J = 6.2 Hz, NHC$H_2$$CH_2$), 2.54 (q, J = 7.0 Hz, 8H, C$H_2$$CH_3$), 1.01 (t, J = 7.0 Hz, CH_2CH_3).^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 158.6 (*o*-C_6H_3N), 138.9 (*p*-C_6H_3N), 94.8 (*m*-C_6H_3N), 52.9 (NHC$H_2$$CH_2$), 46.8 (C$H_2$$CH_3$), 39.8 (NHC$H_2$$CH_2$), 11.8 ($CH_2CH_3$). HRMS (Methode) [m/z]: 308.2 (ES+)

Synthesis of L(o-Dpe-Et$_2$)H$_2$ (1m):

Lithium aluminium hydride (133 mg, 3.50 mmol) was added slowly to a stirred solution of N,N'-(oxybis(2,1-phenylene))bis(2-(diethylamino)acetamide) (426 mg, 1.00 mmol) in dry THF (10 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (1 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 200 mg (51 %) of L(o-Dpe-Et$_2$)H$_2$ (**1m**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 6.99 (dt, J = 1,5 Hz, J = 7.7 Hz, 2H, *1*), 6.75-7.20 (m, 4H, *2+3*), 6.58 (dt, J = 1.5 Hz, J = 7.8 Hz, *4*), 4.74 (br, 2H, NH), 3.19 (q, J = 5.5 Hz, 4H, NHC*H*$_2$CH$_2$), 2.68 (t, J = 6.43 Hz, 4H, NHCH$_2$C*H*$_2$), 2.51 (q, J = 7.1 Hz, 8H, C*H*$_2$CH$_3$), 0.97 (t, J = 7.1 Hz, 12H, CH$_2$C*H*$_3$).^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 143.9 (*C*$_6$H$_4$), 140.3 (*C*$_6$H$_4$), 124.2 (*C*$_6$H$_4$), 117.4 (*C*$_6$H$_4$), 116.6 (*C*$_6$H$_4$), 111.3 (*C*$_6$H$_4$), 51.9 (NHCH$_2$*C*H$_2$), 47.0 (*C*H$_2$CH$_3$), 41.5 (NH*C*H$_2$CH$_2$), 12.0 (CH$_2$*C*H$_3$). HRMS (Methode) [m/z]: 399.3 (ES+)

Synthesis of L(o-Dpen-Et$_2$)H$_2$ (1n):

Lithium aluminium hydride (332 mg, 8.75 mmol) was added slowly to a stirred solution of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diethylamino)acetamide) (1.00 g, 2.30 mmol) in dry THF (23 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (2 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 590 mg (63 %) of L(o-Dpen-Et$_2$)H$_2$ (**1n**) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.18-7.09 (m, 4H, C$_6$*H*$_4$), 6.71-6.63 (m, 4H, C$_6$*H*$_4$), 4.58 (t, J = 4.8 Hz , 2H, NH), 3.20-3.13 (m, 4H, NHCH$_2$CH$_2$), 2.78 (s, 4H, C*H*$_2$C*H*$_2$), 2.74 (t, J = 5.8 Hz, 4H, NHCH$_2$C*H*$_2$), 2.58 (q, J = 7.2 Hz, 8H, C*H*$_2$CH$_3$), 1.05 (t, J = 7.2 Hz, 12H, C*H*$_2$CH$_3$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.4 (*C*$_6$H$_4$), 129.4 (*C*$_6$H$_4$), 127.5 (*C*$_6$H$_4$), 126.3 (*C*$_6$H$_4$), 117.0

(C_6H_4), 110.6 (C_6H_4), 51.7 ($NHCH_2CH_2$), 46.7 (CH_2CH_3), 41.3 ($NHCH_2CH_2$), 31.2 (CH_2CH_2), 12.0 (CH_2CH_3). HRMS (Methode) [m/z]: 411.3 (ES+)

Synthesis of L(o-Dpen-^{i}Bu$_2$)H$_2$ (1o):

Lithium aluminium hydride (771 mg, 20.3 mmol) was added slowly to a stirred solution of N,N'-(ethane-1,2-diylbis(2,1-phenylene))bis(2-(diisobutylamino)acetamide) (3.20 g, 5.80 mmol) in dry THF (60 mL) at 0 °C followed by stirring for one hour at room temperature. The mixture was heated to 66 °C overnight, cooled down to room temperature and water (2 mL) was added followed by stirring for 30 minutes. The formed solid was filtered off, washed with THF and the solvent of the filtrate was removed at vacuum to obtain 1.70 g (57 %) of L(o-Dpen-^{i}Bu$_2$)H$_2$ (**1o**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.15 (t, J = 7.6 Hz, 2H, C_6H_4), 6.99 (d, J = 7.4 Hz, 2H, C_6H_4), 6.68-6.63 (m, 4H, C_6H_4), 4.40 (br, 4H, NH), 3.14 (q, J = 4.9 Hz, 4H, $NHCH_2CH_2$), 2.84 (s, 4H, CH_2CH_2), 2.66 (t, J = 5.7 Hz, 4H, $NHCH_2CH_2$), 2.14 (d, J = 7.2 Hz, 8H, $CH_2CH(CH_3)_2$), 1.75 (nonett, 4H, $CH_2CH(CH_3)_2$), 0.88 (d, J = 6.5 Hz, 24H, $CH_2CH(CH_3)_2$).$^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.2 (C_6H_4), 128.6 (C_6H_4), 127.2 (C_6H_4), 125.7 (C_6H_4), 116.8 (C_6H_4), 110.2 (C_6H_4), 63.9 ($CH_2CH(CH_3)_2$), 54.4 ($NHCH_2CH_2$), 41.2 ($NHCH_2CH_2$), 29.2 (CH_2CH_2), 26.6 ($CH_2CH(CH_3)_2$), 21.1 ($CH_2CH(CH_3)_2$). HRMS (Methode) [m/z]: 523.5 (ES+)

Synthesis of L(Pip-Dmp)H$_2$ (2a):

Lithium aluminium hydride (2.28 g, 60.0 mmol) was added slowly to a solution of 2,2'-(piperazine-1,4-diyl)bis(N-(2,6-dimethylphenyl)acetamide) (7.72 g, 60.0 mmol) in THF (50 mL) and the mixture was refluxed for four days. After cooling to room temperature water (40 mL) and NaOH (aq., 2M, 10 mL) were added and the suspension was filtered through a plug of celite. The solvent was removed and the crude product was recrystallized from THF to obtain 2.73 g (57 %) of L(Pip-Dmp)H$_2$ (**2a**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.00 (d, J=7.4 Hz, 4H, *m*-C_6H_3), 6.81 (t, J=7.4 Hz, 2H, *p*-C_6H_3), 3.99 (br, 2H, N*H*), 3.11 (t, J= 5.9, 4H, NHCH_2), 2.63-2.53 (m, 12H, CH_2N(CH_2)$_2$), 2.32 (s, 12H, PhCH_3). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.6 (*i*-C_6H_3), 128.9 (*m*-C_6H_3), 128.4 (*o*-C_6H_3), 121.3 (*p*-C_6H_3), 57.9 (NHCH$_2$C*H*2N), 53.2 (N(C_2H_4)$_2$N), 44.8 (NH*C*H$_2$CH$_2$N), 18.9 (Ph*C*H$_3$). HRMS (Methode) [m/z]: 381.302 (ES+)

Sythesis of L(Et-Dmp)H$_2$ (2b):

1,2-dibromoethane (1.00 g, 5.60 mmol) was slowly added to pure N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine (2.00 g, 11.2 mmol) at 130 °C and the mixture was stirred at this temperature for three hours. The formed sticky residue was dissolved in a mixture of EtOAc (70 mL) and water (70 mL) followed by separation of the organic phase. The crude product was recrystallized in EtOH (30 mL) at -20 °C to obtain 458 mg (21 %) of L(Et-Dmp)H$_2$ (**2b**) as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.02 (d, J= 7.4 Hz, 4H, meta H), 6.83 (t, J= 7.4 Hz, 2H, para H), 3.91 (br, 2H, N*H*), 3.11 (t, J= 5.6 Hz, 4H, CH$_2$C*H*$_2$NHPh), 2.64-2.62 (m, 8H, C*H*$_2$NCH$_3$C*H*$_2$), 2.34 (s, 12H, PhC*H*$_3$), 2.32 (s, 6H, NC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.7 (*i*-C_6H_3), 128.9 (*m*-C_6H_3), 128.7 (*o*-C_6H_3), 121.2 (*p*-C_6H_3), 58.1 (NCH$_2$*C*H$_2$NHPh), 56.2 (N*C*H$_2$*C*H$_2$N), 45.7 (N*C*H$_2$CH$_2$NPh), 42.2 (N*C*H3), 18.8 (Ph*C*H3). HRMS (Methode) [m/z]: 383.316 (ES +)

Sythesis of L(Et-Dipp)H$_2$ (2c):

1,2-dibromoethane (3.70 g, 20.0 mmol) was slowly added to pure N^1-(2,6-diisopropylphenyl)-N^2-methylethane-1,2-diamine (9.40 g, 40.0 mmol) at 100 °C and the mixture was stirred at this temperature for three hours. The formed sticky residue was dissolved in a mixture of EtOAc (100 mL) and NaOH (aq.) (100 mL) followed by separation of the organic phase. Solvent concentration initiates crystal formation and 4.76 g (46 %) of L(Et-Dipp)H$_2$ (**2c**) could be obtained as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.12-7.02 (m, 6H, C_6H_3), 3.33 (sept, J=6.8 Hz, 4H, $CH(CH_3)_2$), 2.98 (t, J= 2.98, 4H, NCH_2CH_2NPh), 2.68-2.64 (m, 8H, $CH_2N(CH_3)CH_2$), 2.33 (s, 6H, NCH_3), 1.25 (d, J=6.8Hz, 24H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 143.9 (*i*-C_6H_3), 142.1 (*o*-C_6H_3), 123.6 (*m*-C_6H_3), 123.4 (*p*-C_6H_3), 58.5 (NCH_2CH_2NPh), 56.4 (NCH_2CH_2N), 49.1 (NCH_2CH_2NPh), 42.5 (NCH_3), 27.7 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$). HRMS (Methode) [m/z]: 495.442 (ES+)

Synthesis of L(Pr-Dmp)H_2 (2d):

N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine (17.0 g, 95.0 mmol), 1,3-dibromopropane (8.90 g, 44.0 mmol) and potassium carbonate (27.0 g, 195 mmol) were suspended in EtOH (150 mL) and refluxed for three days. The solvent was removed and the residue was dissolved in a mixture of EtOAc (100 mL) and water (200 mL) followed by separation of the organic phase. The solvent of the organic phase was removed and HOAc (equal to the amount of unreacted N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine determined by ^{1}H-NMR analysis) as well as EtOAc (100 mL) and water (150 mL) were added to the mixture followed by stirring for one hour. The solvent of the organic phase was removed to obtain 15.2 g (87 %) of L(Pr-Dmp)H_2 (**2d**) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.11 (d, *J*= 7.46Hz, 4H, *m*-C_6H_3), 6.92 (t, *J*=7.46Hz, 2H, *p*-C_6H_3), 3.83 (br, 2H, N*H*), 3.20 (t, *J*= 5.5Hz, 4H, $NHCH_2CH_2N$), 2.68 (t, *J*= 5.5, 4H, $NHCH_2CH_2N$), 2.60 (t, *J*=7.0, 4H, $CH_2CH_2CH_2$), 2.45 (s, 12H, $PhCH_3$), 2.37 (s, 6H, NCH_3), 1.87 (p, *J*= 7.0, 2H, $CH_2CH_2CH_2$). $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.4 (*i*-C_6H_3), 128.5 (*m*-C_6H_3), 128.1 (*o*-C_6H_3), 120.8 (*p*-C_6H_3), 57.4 ($NHCH_2CH_2N$), 55.9 ($CH_2CH_2CH_2$), 45.3 ($NHCH_2CH_2N$), 41.1(NCH_3), 25.1 ($CH_2CH_2CH_2$), 18.5 ($PhCH_3$). HRMS (Methode) [m/z]: 397.333 (ES +)

Sythesis of L(Bu-Dipp)H_2 (2e):

1,3-dibromopropane (3.03 g, 15.0 mmol) was slowly added to pure N^1-(2,6-diisopropylphenyl)-N^2-methylethane-1,2-diamine (7.03 g, 30.0 mmol) at 100 °C and the

mixture was stirred at this temperature for overnight. The formed solid residue was dissolved in a mixture of EtOAc (50 mL), NaOH (10 g) and water (50 mL) followed by extracting of the aqueous phase with EtOAc (2x50 mL). The combined organic phases were dried over Na_2SO_4 followed by solvent removal. The crude product was crystallized from EtOH (10 mL) at -16 °C to obtain 2.50 g (33 %) of L(Bu-Dipp)H_2 (**2e**) as white crystals.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.12-7.10 (m, 4H , *m*-C_6H_3), 7.06-7.03 (m, 2H, *p*-C_6H_3), 3.78 (br, 2H, N*H*), 3.35 (sept, J=6.8 Hz, 4H, C*H*$(CH_3)_2$), 2.99 (t, J= 5.6 Hz, 4H, NHCH_2C*H*$_2$), 2.62 (t, J=5.6 Hz, 4H, NHC*H*$_2$CH_2), 2.52-2.49 (m, 4H, NC*H*$_2$CH_2C*H*$_2$N), 2.29 (s, 6H, NC*H*$_3$), 1.79 (p, J=7.3 Hz, 2H, NCH_2C*H*$_2$CH_2N), 1.28-1.26 (d, J=6.8, 24H, CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 144.0 (*i*-*C*$_6H_3$), 142.0 (*o*-*C*$_6H_3$), 123.6 (*m*-*C*$_6H_3$), 123.3 (*p*-*C*$_6H_3$), 58.2 (NHCH_2*C*H_2), 56.5 (NH*C*H_2CH_2), 49.1 (N*C*H_2CH_2*C*H_2N), 41.9 (N*C*H_3), 27.6 (*C*H$(CH_3)_2$), 25.9 (NCH_2*C*H_2CH_2N), 24.5 (CH(*C*$H_3)_2$). HRMS (Methode) [m/z]: 509.458 (ES+)

Synthesis of L(Xyl-Dmp)H_2 (2f):

N^1-(2,6-dimethylphenyl)-N^2-methylethane-1,2-diamine (7.13 g, 40.0 mmol), m-xylylene dichloride (3.50 g, 20.0 mmol) and potassium carbonate (8.29 g, 60.0 mmol) were suspended in EtOH (100 mL) and refluxed for four days. The solvent was removed and the resulting residue was dissolved in a mixture of EtOAc (100 mL) and water (100 mL) followed by washing of the organic phase with saturated NaCl (aq.) (20 mL) solution. The organic phase was dried over Na_2SO_4 and the solvent was removed to obtain 8.70 g (95 %) of Synthesis of L(Xyl-Dmp)H_2 (**2f**) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.33-7.23 (m, 4H, Xylyl), 6.99 (d, J=7.52, 4H, *m*-C_6H_3), 6.79 (t, J=7.52, 2H, *p*-C_6H_3), 4.28 (br, 2H, N*H*), 3.59 (s, 4H, C*H*$_2$PhC*H*$_2$), 3.14 (t, J= 5.8Hz, 4H, NCH_2C*H*$_2$NHPh), 2.65 (t, J=5.8, 4H, NC*H*$_2$CH_2NHPh), 2.31 (s, 12H, PhC*H*$_3$), 2.21 (s, 6H, NC*H*$_3$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 146.8 (*i*-C_6H_3), 138.9 (2), 129.8 (*m*-C_6H_3), 128.8 (1), 128.5 (*o*-C_6H_3), 128.3 (4), 127.8 (3), 121.1 (*p*-C_6H_3), 62.8 (*C*H_2PhCH2), 57.4 (N*C*H_2CH_2NHPh), 45.7 (NCH_2*C*H_2NHPh), 41.5 (N*C*H_3), 18.9 (Ph*C*H_3). HRMS (Methode) [m/z]: 459.348 (ES+)

Sythesis of L(Xyl-Dipp)H_2 (2g):

N^1-(2,6-diisopropylphenyl)-N^2-methylethane-1,2-diamine (9.40 g, 40.0 mmol), *m*-xylylene dichloride (3.50 g, 20.0 mmol) and potassium carbonate (8.29 g, 60.0 mmol) were suspended in EtOH (100 mL) and refluxed for four days. The solvent was removed and the resulting residue was dissolved in a mixture of EtOAc (100 mL) and water (100 mL) followed by washing of the organic phase with saturated NaCl (aq.) (20 mL) solution. The organic phase was dried over Na_2SO_4 and the solvent was removed to obtain 11.3 g (99 %) of L(Xyl-Dipp)H_2 (**2g**).

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 7.32-7.03 (m, 10H, C_6H_3+C_6H_4), 3.60 (s, 2H, PhCH_2), 3.35 (sept, J=6.8 Hz, 6H, CH(CH_3)$_2$ + NH), 3.03 (t, J=5.6 Hz, 4H, NHC$H_2$$CH_2$), 2.69 (t, J=5.6Hz, 4H, NHCH_2CH_2), 2.21 (s, 6H, NCH_3), 1.24 (d, J=6.8Hz, 24H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 144.0 (*i*-C_6H_3), 142.0 (*o*-C_6H_3),139.2 (2), 129.4 (1), 128.4 (4), 127.7 (3), 123.6 (*m*-C_6H_3), 123.3 (*p*-C_6H_3), 62.8 (PhCH2), 57.9 (NHC$H_2$$CH_2$), 49.0 (NH$CH_2$$CH_2$), 41.8 (N$CH_3$), 27.7 ($CH$($CH_3$)$_2$), 24.5 (CH($CH_3$)$_2$). HRMS (Methode) [m/z]: 571.476 (ES+)

Complex synthesis

Synthesis of 1nMg:

Mg(HMDS)$_2$ (485 mg, 1.40 mmol) was added to a stirred solution of **1n** (275 mg, 0.67 mmol) in toluene (8 mL) and stirred at 110 °C overnight resulting in a pale brown solution. After cooling to room temperature the solvent was removed and the brown solid was washed with *n*-pentane (1 × 10 mL). The solid was dissolved in THF (5 mL), filtered off and a few drops of *n*-pentane were added to the solution. After standing at room temperature overnight, **1nMg** (171 mg, 0.40 mmol, 59%) could be isolated as clear colourless crystals.

^{1}H NMR (400 MHz, C_6D_6): *δ* (ppm) = 7.49 (t, *J* = 7.5 Hz, 2H, C_6H_4), 7.28 (d, *J* = 7.3 Hz, 2H, C_6H_4), 6.78–6.75 (m, 4H, C_6H_4), 3.55–3.47 (m, 2H, $C_6H_4CH_2CH_2C_6H_4$), 3.34–3.30 (m, 2H, $NCH_2CH_2NC_6H_4$), 3.04–2.96 (m, 2H, $NCH_2CH_2NC_6H_4$), 2.86–2.77 (m, 2H, $C_6H_4CH_2CH_2C_6H_4$), 2.43–2.15 (m, 10H, $NCH_2CH_2NC_6H_4$ + NCH_2CH_3), 2.06–1.97 (m, 2H, $NCH_2CH_2NC_6H_4$), 0.51

(t, *J* = 7.2 Hz, 6H, NCH_2CH_3), 0.38 (t, *J* = 7.2 Hz, 6H, NCH_2CH_3); ^{1}H NMR (400 MHz, THF-d_8): δ (ppm) = 6.87 (dt, *J* = 8.0 Hz, 2H, C_6H_4), 6.79 (dd, *J* = 7.1 Hz, 2H, C_6H_4), 6.28 (d, *J* = 8.0 Hz, 2H, C_6H_4), 6.16 (dt, *J* = 7.2 Hz, 2H, C_6H_4), 3.41–3.28 (m, 4H, $C_6H_4CH_2CH_2C_6H_4$ + $NCH_2CH_2NC_6H_4$), 3.13–2.97 (m, 6H, $NCH_2CH_2NC_6H_4$), 2.87 (q, 8H, *J* = 7.1 Hz, NCH_2CH_3), 2.40–2.30 (m, 2H, $C_6H_4CH_2CH_2C_6H_4$), 1.03 (t, *J* = 8.3 Hz, 12H, NCH_2CH_3); ^{13}C{H} NMR (101 MHz, C_6D_6): δ (ppm) = 156.6 (C_6H_4), 130.4 (C_6H_4), 128.7 (C_6H_4), 126.8 (C_6H_4), 112.5 (C_6H_4), 110.7 (C_6H_4), 52.7 ($C_6H_4CH_2CH_2C_6H_4$), 45.0 (NCH_2CH_2N), 45.0 (NCH_2CH_2N), 39.2 (NCH_2CH_3), 33.8 (NCH_2CH_3), 8.6 (NCH_2CH_3), 8.5 (NCH_2CH_3); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3048 (w), 2966 (w), 2925 (w), 2865 (w), 2795 (w), 1590 (m), 1486 (m), 1440 (m), 1304 (s), 1155 (m), 1083 (m), 746 (s), 728 (vs); anal. calc. (found) for [$C_{26}H_{40}MgN_4$]: C 72.13 (72.23), H 9.31 (8.91), N 12.94 (12.75).

Synthesis of 1nZn:

$Zn(Et)_2$ (1.20 mL, 1.20 mmol, 1.0 M in hexanes) was added to a stirred solution of **1n** (235 mg, 0.57 mmol) in toluene (8 mL) and stirred at 100 °C overnight resulting in a yellow suspension. After cooling to room temperature the solids were filtered off and the filtrate concentrated to 5 mL. After standing at room temperature overnight, **1nZn** (195 mg, 0.41 mmol, 72%) was isolated as clear colourless crystals.

^{1}H NMR (400 MHz, C_6D_6 + THF-d_8): δ (ppm) = 7.25 (t, *J* = 7.5 Hz, 2H, C_6H_4), 7.08 (d, *J* = 7.1 Hz, 2H, C_6H_4), 6.64 (d, *J* = 8.2 Hz, 2H, C_6H_4), 6.55 (t, *J* = 7.2 Hz, 2H, C_6H_4), 3.96–3.89 (m, 2H, $C_6H_4CH_2CH_2C_6H_4$), 3.42–3.37 (m, 2H, $NCH_2CH_2NC_6H_4$), 3.06–2.98 (m, 2H, $NCH_2CH_2NC_6H_4$), 2.56–2.24 (m, 14H, $C_6H_4CH_2CH_2C_6H_4$ + $NCH_2CH_2NC_6H_4$ + NCH_2CH_3), 0.57 (br, 12H, NCH_2CH_3); ^{13}C{H} NMR (101 MHz, C_6D_6 + THF-d_8): δ (ppm) = 154.8 (C_6H_4), 130.5 (C_6H_4), 128.1 (C_6H_4), 126.6 (C_6H_4), 112.8 (C_6H_4), 111.8 (C_6H_4), 53.1 ($C_6H_4CH_2CH_2NC_6H_4$), 47.2 (NCH_2CH_3), 46.0 (NCH_2CH_2N), 40.9 (NCH_2CH_3), 33.5 (NCH_2CH_2N), 8.1 ($ZnCH_2CH_3$), 6.5 ($ZnCH_2CH_3$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3039 (w), 2931 (w), 2867 (w), 2799 (w), 1588 (m), 1473 (m), 1439 (m), 1306 (vs), 1085 (m), 924 (m), 745 (vs), 726 (vs); anal. calc. (found) for [$C_{26}H_{40}ZnN_4$]: C 65.88 (65.88), H 8.51 (8.40), N 11.82 (11.70).

Synthesis of 1jAlH$_2$:

A solution of **1j** (1.84 g, 6.00 mmol) in THF (60 mL) was cooled to −78 °C before it was added to AlH_3·NMe_3 (1.13 g, 12.6 mmol) followed by stirring at room temperature for 15 hours. The solvent was removed and the resulting solid was dried in vacuum to obtain **1jAlH$_2$** (2.00 g, 0.55 mmol, 92%) as a white powder. Crystals suitable for an XRD analysis were obtained from a saturated THF solution upon standing at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.92 (t, J = 7.9 Hz, 1H, C_6H_4), 5.90 (dd, J = 7.9; 2.1 Hz, 2H, C_6H_4), 5.77 (s, 1H), 3.90 (br, 4H, AlH_2), 3.21 (t, J = 5.8 Hz, 4H, NCH_2CH_2N), 3.07–2.95 (m, 8H, NCH_2CH_3), 2.91–2.79 (m, 4H, NCH_2CH_2N), 1.17 (t, J = 7.2 Hz, 12H, NCH_2CH_3); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.9 (C_6H_4), 129.4 (C_6H_4), 101.9 (C_6H_4), 98.02 (C_6H_4), 53.0 (CH_2CH_2), 43.9 (CH_2CH_2), 42.1 (CH_3CH_2), 8.5 (CH_3CH_2); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2967 (w), 2924 (w), 2866 (w), 2804 (w), 1808 (m), 1780 (m), 1579 (m), 1466 (m), 1353 (m), 1264 (m), 1014 (m), 778 (s), 658 (vs), 535 (vs); anal. calc. (found) for [$C_{18}H_{36}N_4Al_2$·0.15 THF]: C 60.39 (60.73), H 10.14 (10.50), N 13.81 (14.13).

Synthesis of 1kAlH$_2$:

A solution of **1k** (330 mg, 1.00 mmol) in THF (15 mL) was cooled to −78 °C before it was added to AlH_3·NMe_3 (180 mg, 2.00 mmol) followed by stirring at room temperature for 1 hour. Upon standing at room temperature crystals of **1kAlH$_2$** (382 mg, 0.99 mmol, 99%) formed, which were collected and dried in vacuum.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.98–6.91 (m, 1H, C_6H_4), 6.00–5.90 (m, 2H, C_6H_4), 5.88–5.80 (m, 1H, C_6H_4), 3.97 (br, 4H, AlH_2), 3.36–3.25 (m, 8H, α-pip + $C_6H_4NCH_2CH_2$), 3.01 (t, J = 6.0 Hz, 4H, $C_6H_4NCH_2CH_2$), 2.34 (dt, J = 11.9 Hz, J = 2.6 Hz, 4H, α-pip), 2.02–1.74 (m, 8H, β-pip), 1.47–1.25 (m, 4H, γ-pip); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.9 (C_6H_4), 129.7 (C_6H_4), 102.1 (C_6H_4), 98.3 (C_6H_4), 59.8 ($C_6H_4NCH_2CH_2$), 54.8 (α-pip), 41.7 ($C_6H_4NCH_2CH_2$), 24.2 (β-pip), 23.4 (γ-pip); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2942 (w), 2856 (w), 1805 (w), 1775 (w), 1590 (m), 1469 (m), 1339 (m), 1229 (m), 1029 (m), 777 (s), 674 (vs); despite repeated attempts no suitable elemental analysis could be obtained.

Synthesis of 1mSnHMDS:

$Sn(HMDS)_2$ (706 mg, 0.62 mL, 1.61 mmol) was added to a stirred solution of **1m** (320 mg, 0.80 mmol) in toluene (8 mL) followed by stirring at 100 °C overnight resulting in a black solution. After cooling to room temperature the solvent was removed and *n*-pentane (5 mL) was added to the black oil resulting in the instant formation of crystals. After washing the crystals with *n*-pentane (3 × 2 mL), **1mSn** (110 mg, 0.12 mmol, 14%) could be isolated as slightly brownish crystals.

^{1}H NMR (400 MHz, 353 K, toluene-d_8): δ (ppm) = 7.22–7.20 (m, 1H, C_6H_4), 7.04–7.00 (m, 3H, C_6H_4), 6.68–6.64 (m, 2H, C_6H_4), 6.52–6.41 (m, 2H, C_6H_4), 3.37–3.23 (m, 4H, NCH_2CH_2N), 2.74–2.58 (m, 8H, NCH_2CH_2N + NCH_2CH_3), 2.51–2.42 (m, 4H, NCH_2CH_3), 0.89–0.79 (m, 12H, NCH_2CH_3), 0.26–0.22 (m, 36H, $SiCH_3$); $^{13}C\{^1H\}$ NMR: even after repeated attempts at various temperatures no suitable ^{13}C NMR spectrum could be obtained; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3052 (vw), 2944 (w), 2894 (vw), 2865 (w), 2831 (w), 1594 (m), 1491 (s), 1305 (s), 1243 (s), 1126 (m), 930 (vs), 732 (vs), 662 (s); anal. calc. (found) for [$C_{36}H_{72}N_6OSi_4Sn_2$]: C 45.29 (45.46), H 7.60 (7.11), N 8.80 (8.69).

Synthesis of 1nSnHMDS:

$Sn(HMDS)_2$ (503 mg, 0.44 mL, 1.14 mmol) was added to a stirred solution of **1n** (235 mg, 0.57 mmol) in toluene (8 mL) followed by stirring at 100 °C overnight resulting in an orange solution and a grey precipitate. After cooling to room temperature the solids were filtered off and the filtrate was concentrated to dryness affording a dark orange solid. *n*-pentane (5 mL) was added causing the instant formation of **1nSn** (225 mg, 0.23 mmol, 41%) as an orange crystalline solid. Crystals suitable for an X-Ray diffraction analysis were obtained from recrystallization in a mixture of THF/*n*-pentane (1 : 1) at room temperature.

^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.55 (d, J = 6.1 Hz, 2H, C_6H_4), 7.36 (t, J = 7.4 Hz, 2H, C_6H_4), 6.96 (t, J = 6.9 Hz, 2H, C_6H_4), 6.89 (d, J = 8.1 Hz, 2H, C_6H_4), 3.64 (s, 4H, $C_6H_4CH_2CH_2C_6H_4$), 3.29–3.26 (m, 4H, NCH_2CH_2N), 2.48–2.45 (m, 12H, NCH_2CH_2N + NCH_2CH_3), 0.60 (t, J = 7.3 Hz, 12H, NCH_2CH_3), 0.36 (s, 36H, $SiCH_3$); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ (ppm) = 154.4 (C_6H_4),

130.0 (C_6H_4), 127.5 (C_6H_4), 116.7 (C_6H_4), 115.6 (C_6H_4), 54.0 ($C_6H_4CH_2CH_2C_6H_4$), 49.8 (NCH_2CH_2N), 43.9 (NCH_2CH_2N), 36.1 (NCH_2CH_3), 8.6 (NCH_2CH_3), 6.8 ($SiCH_3$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3057 (vw), 2945 (w), 2892 (vw), 2826 (w), 1591 (m), 1483 (m), 1438 (m), 1243 (s), 904 (vs), 821 (vs), 744 (s), 664 (s); anal. calc. (found) for [$C_{38}H_{76}N_6Si_4Sn_2 \cdot 0.15\ C_5H_{12}$]: C 47.61 (47.83), H 8.02 (7.67), N 8.60 (8.51).

Synthesis of 2bMg:

$Mg(HMDS)_2$ (1.57 g, 4.56 mmol) was added to a stirred solution of **2b** (830 mg, 2.17 mmol) in toluene (8 mL) and stirred at 100 °C overnight resulting in the formation of a white precipitate. After cooling to room temperature, the solids were filtered off and washed with *n*-pentane (3 × 5 mL) to obtain **2bMg** (570 mg, 1.40 mmol, 65%) as a white solid. Crystals suitable for an X-Ray diffraction analysis were obtained by extraction with hot THF (40 mL) followed by slow cooling to room temperature.

^1H NMR (400 MHz, THF-d_8): δ (ppm) = 6.66 (d, J = 7.3 Hz, 4H, *m*-C_6H_3), 6.22 (t, J = 7.2 Hz, 2H, *p*-C_6H_3), 3.09–2.92 (m, 6H, $NCH_2CH_2NC_6H_3$), 2.89–2.82 (m, 2H, NCH_2CH_2N), 2.59 (s, 6H, NCH_3) 2.57–2.53 (m, 2H, $NCH_2CH_2NC_6H_3$), 2.19 (s, 12H, $CH_3C_6H_3$); $^{13}C\{^1H\}$ NMR: due to the low solubility of the complex, even after extended scans no suitable ^{13}C NMR spectrum could be obtained; IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3045 (w), 2965 (w), 2804 (w), 2788 (w), 1588 (m), 1470 (m), 1415 (m), 1280 (m), 1074 (m), 760 (vs), 740 (s); anal. calc. (found) for [$C_{24}H_{36}MgN_4$]: C 71.20 (71.13), H 8.96 (8.63), N 13.84 (13.72).

Synthesis of 2aZnEt:

$Zn(Et)_2$ (2.43 mL, 2.43 mmol, 1.0 M in hexanes) was added to a stirred solution of **2a** (440 mg, 1.16 mmol) in toluene (8 mL) and stirred at 100 °C overnight resulting in a clear solution. Upon slow cooling to room temperature **2aZn** (140 mg, 0.25 mmol, 21%) crystallized as clear colorless blocks.

^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.27 (d, J = 7.4 Hz, 4H, p-C_6H_3), 7.02 (t, J = 7.5 Hz, 2H, m-C_6H_3), 3.07 (t, J = 5.4 Hz, 4H, NCH_2CH$_2$NC$_6$H$_3$), 2.48 (s, 12H, CH_3C$_6$H$_3$), 3.35 (d, J = 8.8 Hz, 4H, NCH_2CH$_2$N), 2.13 (t, J = 5.4 Hz, 4H, NCH_2CH$_2$NC$_6$H$_3$), 1.99 (d, J = 8.8 Hz, 4H, NCH_2CH$_2$N), 1.32 (t, J = 8.0 Hz, 6H, ZnCH$_2$CH_3), 0.38 (q, J = 8.1 Hz, 4H, ZnCH_2CH$_3$); ^{13}C{H} NMR (101 MHz, C_6D_6): δ (ppm) = 154.9 (i-C_6H_3), 133.3 (o-C_6H_3), 129.3 (m-C_6H_3), 121.2 (p-C_6H_3), 62.3 (NCH$_2$CH$_2$NC$_6$H$_3$), 52.0 (NCH$_2$CH$_2$N), 48.0 (NCH$_2$CH$_2$NC$_6$H$_3$), 20.4 (CH$_3$C$_6$H$_3$), 12.3 (ZnCH$_2$CH$_3$), 3.6 (ZnCH$_2$$CH_3$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3052 (w), 2939 (w), 2893 (w), 2852 (w), 1585 (m), 1460 (m), 1418 (s), 1273 (s), 1087 (s), 955 (s), 755 (vs); anal. calc. (found) for [$C_{28}H_{44}Zn_2N_4$]: C 59.27 (59.59), H 7.82 (7.41), N 9.87 (9.70).

Synthesis of 2aAlMe$_2$:

AlMe$_3$ (2.00 mmol, 1.00 mL, 2.0 M in toluene) was added slowly to a stirred solution of **2a** (382 mg, 1.00 mmol) in toluene (10 mL) and stirred at reflux overnight. Upon slow cooling to room temperature **2aAlMe$_2$** (400 mg, 0.81 mmol, 81%) crystallized as clear colorless crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.06 (d, J = 8.0 Hz, 4H, m-C_6H_3), 6.90 (t, J = 7.5 Hz, 2H, p-C_6H_3), 3.59 (d, J = 9.3 Hz, 4H, NCH_2CH_2N), 3.25 (t, J = 5.7 Hz, 4H, NCH$_2$CH_2NC$_6$H$_3$), 3.13 (t, J = 5.7 Hz, 4H, NCH_2CH$_2$NC$_6$H$_3$), 2.99 (d, J = 9.1 Hz, 4H, NCH_2CH_2N), 2.31 (s, 12H, C$_6$H$_3$CH_3), −0.74 (s, 12H, Al(CH_3)$_2$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.1 (i-C_6H_3), 137.8 (o-C_6H_3), 128.3 (m-C_6H_3), 123.2 (p-C_6H_3), 61.4 (NCH$_2$CH$_2$NC$_6$H$_3$), 51.7 (NCH$_2$$CH_2NC_6H_3$), 45.8 (NC$H_2CH_2$N), 19.0 (C$_6H_3CH_3$), −6.9 (Al(C$H_3$)$_2$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2935 (w), 2916 (w), 2838 (w), 2809 (w), 1466 (m), 1229 (m), 1184 (m), 1095 (m), 944 (m), 886 (m), 653 (s); anal. calc. (found) for [$C_{28}H_{47}N_4Al_2$·0.15 C_7H_8]: C 68.89 (68.96), H 9.39 (9.44), N 11.06 (11.22).

Synthesis of 2bZn:

Zn(Et)$_2$ (5.10 mL, 5.10 mmol, 1.0 M in hexanes) was added to a stirred solution of **2b** (930 mg, 2.43 mmol) in toluene (8 mL) and stirred at 100 °C overnight resulting in a clear solution.

Upon slow cooling to room temperature **2bZn** (890 mg, 2.00 mmol, 82%) crystallized as clear colourless blocks.

^{1}H NMR (400 MHz, C_6D_6 + THF-d_8): δ (ppm) = 6.99 (d, J = 7.3 Hz, 4H, m-C_6H_3), 6.71 (t, J = 7.4 Hz, 2H, p-C_6H_3), 3.34–3.28 (m, 2H, NCH_2CH$_2$NC$_6$H$_3$), 2.83–2.77 (m, 2H, NCH_2CH$_2$NC$_6$H$_3$), 2.37–2.35 (m, 2H, NCH_2CH$_2$N), 2.28–2.17 (m, 4H, NCH_2CH$_2$NC$_6$H$_3$), 2.14–2.12 (m, 18H, NCH_3 + CH_3C$_6$H$_3$), 1.80–1.77 (m, 2H, NCH_2CH$_2$N); ^{13}C{H} NMR (101 MHz, C_6D_6 + THF-d_8): δ (ppm) = 156.9 (i-C_6H_3), 133.6 (o-C_6H_3), 128.6 (m-C_6H_3), 119.4 (p-C_6H_3), 61.2 (CH$_3$NCH$_2$$CH_2NCH_3$), 51.3 (NCH$_2$$CH_2$N), 50.1 (NCH$_2$$CH_2$N), 44.3 ($CH_3NCH_2CH_2NCH_3$), 20.4 ($CH_3C_6H_3$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3046 (w), 2966 (w), 2853 (w), 2836 (w), 1587 (m), 1469 (m), 1412 (m), 1279 (m), 1084 (m), 764 (vs), 740 (s); anal. calc. (found) for [$C_{24}H_{36}ZnN_4$]: C 64.64 (64.59), H 8.14 (7.70), N 12.56 (12.30).

Synthesis of 2bAlH:

A solution of **2b** (300 mg, 0.78 mmol) in Et_2O (10 mL) was cooled to −78 °C before it was added to AlH_3·NMe_3 (77 mg, 0.86 mmol) followed by stirring at room temperature overnight. The solvent was removed and the resulting crystalline solid was washed with *n*-pentane (2 × 5 mL) to obtain **2bAlH** (298 mg, 0.73 mmol, 93%) as a white crystalline solid.

^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.07–7.02 (m, 4H, m-C_6H_3), 6.97–6.93 (m, 2H, p-C_6H_3), 3.13–3.06 (m, 2H, NCH_2CH$_2$NC$_6$H$_3$), 2.61–2.50 (m, 4H, NCH_2CH$_2$N + NCH_2CH$_2$NC$_6$H$_3$), 2.46 (s, 6H, NCH_3), 2.11–2.04 (m, 2H, NCH_2CH$_2$N), 1.99 (s, 6H, C$_6$H$_3$CH_3), 1.96 (s, 6H, C$_6$H$_3$CH_3), 1.94–1.91 (m, 2H, NCH_2CH$_2$NC$_6$H$_3$), 1.77–1.70 (m, 2H, NCH_2CH$_2$NC$_6$H$_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.75–6.66 (m, 6H, C$_6$$H_3$), 3.21–3.15 (m, 2H, NC$H_2CH_2NC_6H_3$), 3.08–2.98 (m, 4H, NC$H_2CH_2$N + NC$H_2CH_2NC_6H_3$), 2.83–2.75 (m, 2H, NC$H_2CH_2$N), 2.64–2.60 (m, 4H, NC$H_2CH_2NC_6H_3$), 2.55 (s, 6H, NCH$_3$), 2.10 (s, 6H, C$_6H_3CH_3$), 1.76 (s, 6H, C$_6H_3CH_3$); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ (ppm) = 153.0 (i-C_6H_3), 137.5 (o-C_6H_3), 128.4 (m-C_6H_3), 122.6 (p-C_6H_3), 58.8 (NCH$_2$$CH_2NC_6H_3$), 54.5 (N$CH_2$$CH_2$N), 47.8 (N$CH_2CH_2NC_6H_3$), 41.0 (N$CH_3$), 20.6 (C$_6H_3$$CH_3$), 18.5 (C$_6H_3$$CH_3$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2956 (w), 2910 (w), 2861 (w), 2806 (w), 1753 (w), 1590

(m), 1466 (m), 1339 (s), 1262 (s), 1217 (s), 1092 (s), 920 (m), 758 (vs), 654 (vs); anal. calc. (found) for [C24H37AlN4]: C 70.55 (69.93), H 9.13 (8.66), N 13.71 (13.42).

Synthesis of 2bAlMe$_2$:

$AlMe_3$ (15.7 mmol, 7.85 mL, 2.0 M in toluene) was added slowly to a stirred solution of **2b** (3.00 g, 7.80 mmol) in toluene (35 mL) and stirred under reflux overnight. After cooling to room temperature, the white suspension was filtered and the remaining white solid was dried in vacuum to obtain **2bAlMe$_2$** (2.73 g, 5.50 mmol, 70%). Crystals suitable for an XRD analysis grew from the filtrate upon standing at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.07 (d, J = 7.4 Hz, 4H, *m*-C_6H_3), 6.91 (t, J = 7.4 Hz, 2H, *p*-C_6H_3), 3.48–3.30 (m, 6H, NCH_2CH_2N + $NCH_2CH_2NC_6H_3$), 3.01–2.87 (m, 6H, NCH_2CH_2N + $NCH_2CH_2NC_6H_3$), 2.71–2.69 (m, 6H, NCH_3), 2.32 (s, 12H, $C_6H_3CH_3$), −0.72–0.74 (m, 6H, $Al(CH_3)_2$), −0.79–0.81 (m, 6H, $Al(CH_3)_2$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) = 149.3 (i-C_6H_3), 138.0 (*o*-C_6H_3), 128.3 (*m*-C_6H_3), 123.2 (*p*-C_6H_3), 61.2 ($NCH_2CH_2NC_6H_3$), 54.2 (NCH_2CH_2N), 46.5 ($NCH_2CH_2NC_6H_3$), 40.3 (NCH_3), 18.9 ($C_6H_3CH_3$),–7.4 ($Al(CH_3)_2$), −9.00 ($Al(CH_3)_2$); IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2922 (w), 2796 (w), 1589 (vw), 1471 (m), 1263 (m), 1215 (m), 1107 (m), 953 (m), 886 (s), 769 (s), 648 (vs); anal. calc. (found) for [$C_{28}H_{48}N_4Al_2$·0.11 C_7H_8]: C 67.98 (68.68), H 9.78 (9.67), N 11.33 (11.35).

Synthesis of 2dAlMe$_2$:

$AlMe_3$ (5.00 mmol, 2.50 mL, 2.0 M in toluene) was added slowly to a stirred solution of **2d** (970 mg, 2.45 mmol) in toluene (20 mL) and stirred under reflux overnight. After cooling to room temperature, the solution was concentrated to about 6 mL to initiate crystallization. After standing at room temperature overnight **2dAlMe$_2$** (710 mg, 1.22 mmol, 50%) was isolated as clear colourless crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.06 (d, J = 7.4 Hz, 4H, *m*-C_6H_3), 6.90 (t, J = 7.4 Hz, 2H, *p*-C_6H_3), 3.46–3.38 (m, 2H, $NCH_2CH_2NC_6H_3$), 3.33–3.25 (m, 2H, $NCH_2CH_2CH_2N$), 3.03–2.79 (m,

6H, NC*H*$_2$C*H*$_2$NC$_6$H$_3$ + NC*H*$_2$CH$_2$C*H*$_2$N), 2.67–2.61 (m, 8H, NC*H*$_2$C*H*$_2$NC$_6$H$_3$ + NC*H*$_3$), 2.32 (s, 12H, C$_6$H$_3$C*H*$_3$), 2.21–2.11 (m, 2H, CH$_2$C*H*$_2$CH$_2$) −0.78–0.81 (m, 12H, Al(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ (ppm) = 149.6 (i-*C*$_6$H$_3$), 138.1 (*o*-*C*$_6$H$_3$), 128.2 (*m*-*C*$_6$H$_3$), 123.0 (*p*-*C*$_6$H$_3$), 60.4/59.4 (NCH$_2$*C*H$_2$NC$_6$H$_3$), 56.4/56.1, (*C*H$_2$CH$_2$*C*H$_2$), 46.8/46.7 (N*C*H$_2$CH$_2$NC$_6$H$_3$), 40.2/40.0 (N*C*H$_3$), 22.6/20.4 (CH$_2$*C*H$_2$CH$_2$) 18.9/18.9 (C$_6$H$_3$*C*H$_3$), −8.0 /-9.0 (Al(*C*H$_3$)$_2$); IR (ATR): ~ν [cm^{-1}] = 2913 (w), 2812 (w), 1474 (m), 1422 (m), 1338 (m), 1236 (m), 1103 (m), 936 (m), 654 (vs), 566 (s); anal. calc. (found) for [C$_{29}$H$_{50}$N$_4$Al$_2$]: C 68.47 (68.50), H 9.91 (9.62), N 11.01 (10.85).

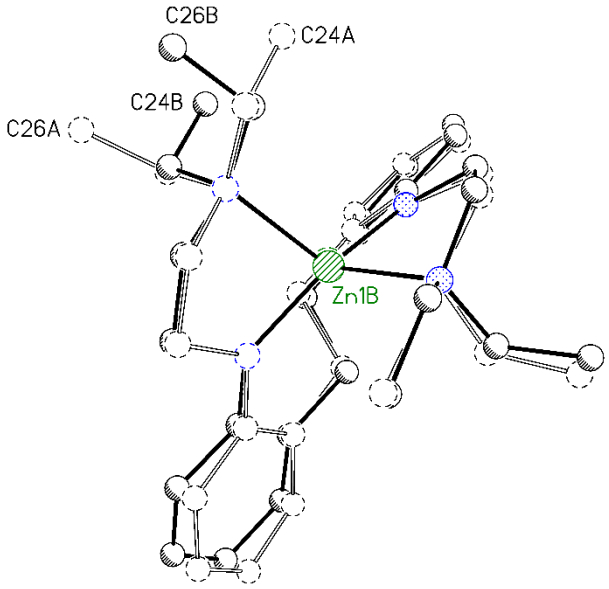

Figure S1 Fit of the two symmetry-independent molecules of 1nZn as observed by X-ray diffraction analysis.

Crystallographic details

The intensity data were collected on a GV-50 diffractometer with TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying Cu-K$_\beta$ radiation (λ = 1.39222 Å) for **1mSnHMDS** and **1nZn** and Cu-K$_\alpha$ radiation (λ = 1.54184 Å) for all other

compounds. Analytical absorption corrections were applied to the data.[S11] The structures were solved by direct methods (SHELXT)[S12] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-2018).[S13] The hydrogen atoms bonded to the Aluminium-ion of **1jAlH2**, **1kAlH2**, **2bAlH2** and to the amine groups of compound **2a** and **2b** were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[S13] Crystallographic data as well as structure solution and refinement details are summarized in Table S1 of the ESI. Olex2 was used for structure representations.[S14]

Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2026438 for **1jAlH$_2$**, CCDC-2026439 for **1kAlH$_2$**, CCDC-2026440 for **1mSnHMDS**, CCDC-2026441 for **1nMg**, CCDC-2026442 for **1nSnHMDS**, CCDC-2026443 for **1nZn**, CCDC-2026444 for **2a**, CCDC-2026430 for **2aAlMe$_2$**, CCDC-2026431 for **2aZnEt**, CCDC-2026432 for **2b**, CCDC-2026433 for **2bAlH**, CCDC-2026434 for **2bAlMe$_2$**, CCDC-2026435 for **2bMg**, CCDC-2026436 for **2bZn**, and CCDC-2026437 for **2dAlMe$_2$**.

Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**1jAlH2**	**1kAlH2**	**1mSnHMDS**	**1nMg**
formula	$C_{18}H_{36}Al_2N_4$	$C_{22}H_{40}Al_2N_4O_{0.50}$	$C_{36}H_{72}N_6OSi$	$C_{26}H_{40}MgN_4$
fw ($g \cdot mol^{-1}$)	362.47	422.54	954.73	432.93
T/°C	-140(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	monoclinic	orthorhomb	orthorhombic
space group	P $2_1/c$	P $2_1/c$	P 2_1 2_1 2_1	P n a 2_1
a/ Å	13.2404(3)	12.0676(3)	13.8445(2)	18.2567(3)
b/ Å	14.7403(3)	13.4021(3)	17.9944(2)	11.3141(2)
c/ Å	12.6651(4)	15.1427(3)	18.8137(2)	11.7597(2)
α/°	90	90	90	90
β/°	117.329(4)	95.948(2)	90	90
γ/°	90	90	90	90
V/Å^3	2195.92(12)	2435.86(10)	4686.93(10)	2429.06(7)
Z	4	4	4	4
ρ ($g \cdot cm^{-3}$)	1.096	1.152	1.353	1.184
μ (cm^{-1})	12.34	11.97	72.95	7.68
measured data	12578	14061	30878	15495
data with I > 2σ(I)	3807	4327	9096	4244
unique data (R_{int})	4365/0.0263	4836/0.0281	9256/0.028	4291/0.0202
wR_2 (all data, on	0.0976	0.1107	0.0431	0.0643
R_1 ($I > 2\sigma(I)$) [a]	0.0336	0.0403	0.0178	0.0242
S [b]	1.034	1.067	1.040	1.037
Res. dens./e·Å^{-3}	0.221/-0.186	0.243/-0.271	0.385/-	0.175/-0.139
Flack-parameter	-	-	0.004(2)	0.009(15)
absorpt method	gaussian	gaussian	multi-scan	multi-scan
absorpt corr	0.951/0.977	0.965/0.975	0.575/1.000	0.955/1.000
CCDC No.	2026438	2026439	2026440	2026441

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**1nSnHMDS**	**1nZn**	**2a**	**2aAlMe2**
formula	$C_{38}H_{76}N_6Si_4Sn_2$	$C_{26}H_{40}N_4Zn$	$C_{24}H_{36}N_4$	$C_{28}H_{46}Al_2N_4$
fw ($g \cdot mol^{-1}$)	966.78	473.99	380.57	492.65
°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P $2_1/n$	P $2_1/c$	P $2_1/c$	P $2_1/n$
a/ Å	13.02620(10)	17.1511(1)	8.5472(2)	12.2153(3)
b/ Å	16.2087(2)	21.9866(2)	18.5720(4)	8.4890(3)
c/ Å	33.3195(3)	12.9305(1)	14.0121(3)	13.6679(5)
α/°	90	90	90	90
β/°	96.394(1)	91.116(1)	98.247(2)	92.201(2)
γ/°	90	90	90	90
V/Å^3	6991.24(12)	4875.09(6)	2201.26(9)	1416.26(8)
Z	6	8	4	2
ρ ($g \cdot cm^{-3}$)	1.378	1.292	1.148	1.155
μ (cm^{-1})	97.48	11.17	5.22	10.84
measured data	46347	32011	12964	8174
data with I > 2σ(I)	12581	8895	3268	2443
unique data (R_{int})	13491/0.0293	9646/0.0276	3870/0.0381	2807/0.033
wR_2 (all data, on	0.0559	0.0778	0.1050	0.0962
R_1 ($I > 2\sigma(I)$) [a)]	0.0224	0.0299	0.0402	0.0364
S [b)]	1.025	1.027	1.040	1.025
Res. dens./$e \cdot Å^{-3}$	1.151/-0.596	0.315/-0.390	0.204/-0.188	0.284/-
absorpt method	multi-scan	multi-scan	Gaussian	multi-scan
absorpt corr	0.378/1.000	0.648/1.000	0.878/0.956	0.682/1.000
CCDC No.	2026442	2026443	2026444	2026430

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**2aZnEt**	**2b**	**2bAlH**	**2bAlMe2**
formula	$C_{28}H_{44}N_4Zn_2$	$C_{24}H_{38}N_4$	$C_{24}H_{37}AlN_4$	$C_{28}H_{48}Al_2N_4$
fw ($g \cdot mol^{-1}$)	567.41	382.58	408.55	494.66
°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	P $\bar{1}$	P $2_1/c$	P $2_1/n$	P $2_1/c$
a/ Å	9.2946(3)	8.05464(11)	9.7448(2)	9.4698(3)
b/ Å	10.3097(3)	18.54236(19)	13.2241(2)	12.9516(5)
c/ Å	15.5461(6)	8.27176(10)	18.4085(3)	12.8812(4)
α/°	104.387(3)	90	90	90
β/°	90.487(3)	114.3273(16)	103.626(2)	107.433(4)
γ/°	109.209(3)	90	90	90
V/Å^3	1355.99(8)	1125.71(3)	2305.46(7)	1507.30(9)
Z	2	2	4	2
ρ ($g \cdot cm^{-3}$)	1.390	1.129	1.177	1.090
μ (cm^{-1})	23.33	5.11	8.84	10.19
measured data	17904	34806	20227	7451
data with I > 2σ(I)	4628	2115	3971	2496
unique data (R_{int})	5320/0.0322	2280/0.0381	4615/0.0252	2659/0.026
wR_2 (all data, on	0.0706	0.0918	0.0956	0.1144
R_1 ($I > 2\sigma(I)$) [a]	0.0277	0.0339	0.0368	0.0460
S [b]	1.044	1.031	1.045	1.146
Res. dens./$e \cdot Å^{-3}$	0.342/-0.447	0.220/-0.182	0.236/-0.238	0.226/-
absorpt method	multi-scan	gaussian	gaussian	analytical
absorpt corr	0.767/1.000	0.866/0.975	0.932/0.970	0.840/0.922
CCDC No.	2026431	2026432	2026433	2026434

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**2bMg**	**2bZn**	**2dAlMe2**
formula	$C_{24}H_{36}MgN_4$	$C_{24}H_{36}N_4Zn$	$C_{29}H_{50}Al_2N_4$
fw ($g \cdot mol^{-1}$)	404.88	445.94	508.69
°C	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P $2_1/c$	P $2_1/n$	P $2_1/c$
a/ Å	8.7239(1)	8.66060(10)	31.9265(7)
b/ Å	15.0640(2)	15.1890(2)	7.4319(2)
c/ Å	17.5875(3)	17.3370(2)	13.1546(3)
α/°	90	90	90
β/°	104.291(2)	102.0200(10)	98.015(2)
γ/°	90	90	90
V/$Å^3$	2239.77(6)	2230.61(5)	3090.76(13)
Z	4	4	4
ρ ($g \cdot cm^{-3}$)	1.201	1.328	1.093
μ (cm^{-1})	8.01	11.97	10.06
measured data	14829	14690	11163
data with I > 2σ(I)	4054	4082	4823
unique data (R_{int})	4369/0.0205	4364/0.0180	5946/0.0259
wR_2 (all data, on	0.0875	0.0712	0.1294
R_1 ($I > 2\sigma(I)$) [a]	0.0317	0.0253	0.0448
S [b]	1.027	1.049	1.038
Res. dens./$e \cdot Å^{-3}$	0.227/-0.186	0.310/-0.263	0.394/-0.241
absorpt method	multi-scan	multi-scan	gaussian
absorpt corr	0.937/1.000	0.866/1.000	0.963/0.992
CCDC No.	2026435	2026436	2026437

[a] Definition of the *R* indices: $R_1 = (\Sigma || F_o| - |F_c ||)/\Sigma| F_o |$;

$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$;

[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$

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Preface

The following chapter has already been submitted to the New Journal of Chemistry of the Royal Society of Chemistry.

'Synthesis, Structure, and Catalytic Activity of Dinuclear Aluminium Bis(amidinate) and Bis(guanidinate) Complexes´ submitted for publication.

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Author contributions

The manuscript was prepared in equal contributions by the first authors (A. Rösch, F. Seifert). R. Kretschmer supervised the research and revised the manuscript. All ligands as well as complexes were synthesized and characterized (NMR, IR, EA, X-Ray) by A. Rösch supported by V. Vass. All cyclic voltammetric experiments have been performed by A. Rösch. All catalytic experiments and evaluations have been performed by F. Seifert. H. Görls evaluated the single crystal X-Ray diffraction measurements and provided the corresponding section in the Supporting Information.

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5. Synthesis, Structure, and Catalytic Activity of Dinuclear Aluminium Bis(amidinate) and Bis(guanidinate) Complexes

Abstract

*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 ^{1}H, ^{13}C, 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.*

5.1 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(amidine)s[4] 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, Figure 1.

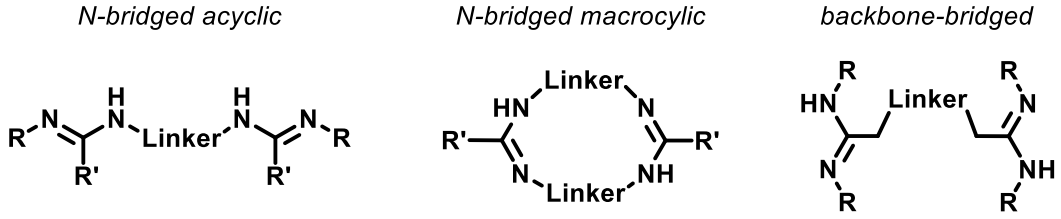


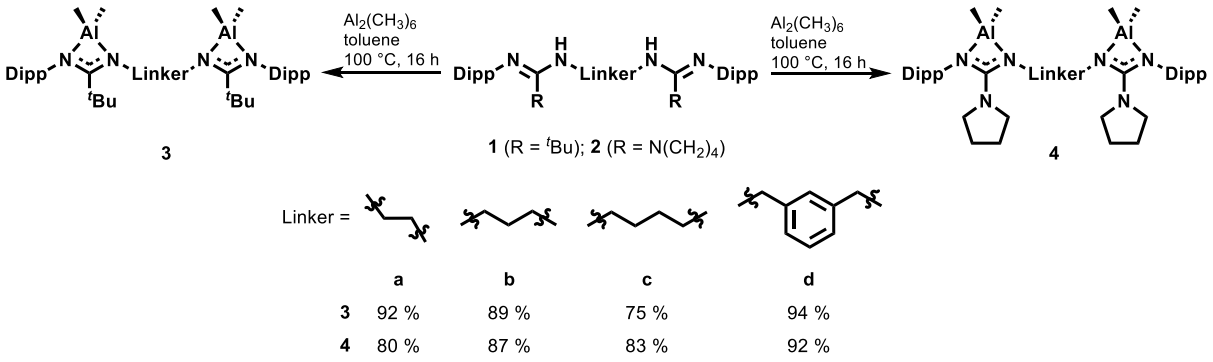
Figure 17. Various types of bis(amidine)s (R'= alky, aryl) and bis(guanidine)s (R'= NR''R''').

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.[6] However, examples incorporating p-block elements remain rare and limited to a few examples.[3,4e,4j,4l,4m,4n,4p,4o,4y,6i,7] In terms

of catalysis, dinuclear aluminium bis(amidinate)s have been applied for the fixation of carbon dioxide into cyclic carbonates[6i] and for the ring-opening polymerization (ROP) of cyclic esters including ε-caprolactone and *L*-lactide.[6h,7c] With respect to the latter, cooperative effects were not observed in case of the backbone-bridged bis(amidinate)s,[7c] likely because of the opposing orientation of the two active sites, while in case of the nitrogen-bridged relatives cooperativity was seen.[6h] However, only two aromatic bridging groups have been studied and experiments in which the metal–metal separation is systematically altered have yet to be performed. 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.

5.2 Results and discussion

Synthesis and structural characterization of dinuclear aluminium complexes



Scheme 4. 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 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,[4ae,5d,8] using protocols established for dinuclear alkyl aluminium bis(β-diketiminate) complexes.[9] 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, ^{1}H and ^{13}C NMR as well as IR spectroscopy. Notably, ^{27}Al NMR resonances could not been detected despite extended numbers of scans. Common features observed in the respective ^{1}H 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.

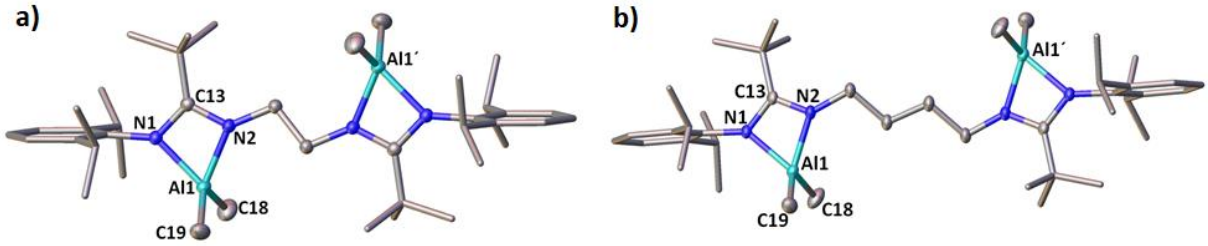


Figure 18. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) of a) **3a** and b) **3b**. Selected bond lengths and angles are given in Table 1.

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 Figure 2 and 3. In case of complex **3d**, the crystals and hence the XRD data were of poor quality, but the connectivity was unambiguously established, Figure S1. The Al–C bond lengths with values in between 1.9507(14) and 1.9692(16) Å are comparable to those reported for other methyl aluminium amidinate (1.937(6) and 1.958(3) Å),[10] guanidinate (1.955(4) and 1.9726(19) Å),[11] bis(amidinate) (1.943(4) and 1.946(4) Å),[4l] and bis(guanidinate) complexes (1.925(7) and 1.962(3) Å).[12] 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**), Table 1 and 2.

Table 1. Selected bond lengths (Å) and angles (°) of the dinuclear aluminium bis(amidinate) complexes.

Compound	bond lengths			bond angles		
	Al–Al	Al–N	Al–R	N–Al–N	N–C–N	R–Al–R
3a	6.2911(7)	1.915(1)-1.9441(10)	1.9507(14)-1.9580(14)	68.27(4)	107.47(9)	117.18(6)
3c	8.1793(6)	1.9196(10)-1.9358(9)	1.9589(13)-1.9599(14)	68.41(4)	107.68(9)	117.56(6)
5a	6.3599(16)	1.872(3)-1.892(3)	2.4902(12)-2.5005(8)	70.55(11)	107.6(3)	113.85(4)
5b	6.4993(18)	1.880(3)-1.896(3)	2.4800(12)-2.5037(9)	70.66(13)-70.71(14)	108.3(3)	111.44(4)-112.07(4)
5c	8.1977(14)	1.869(2)-1.894(2)	2.4816(7)-2.4925(8)	70.60(9)	107.5(2)	112.22(3)
5d	6.903(2)	1.868(4)-1.895(6)	2.4752(15)-2.523(2)	70.21(17)-71.2(2)	106.1(4)-108.4(5)	111.00(6)-111.22(6)
7d	7.4043(5)	1.8667(13)-1.9001(10)	2.0981(6)-2.1143(5)	70.28(5)-70.59(5)	107.08(11)-107.28(12)	110.89(2)-112.79(3)

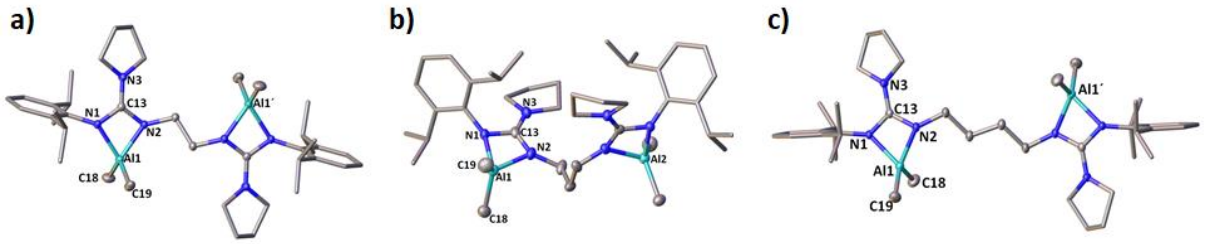
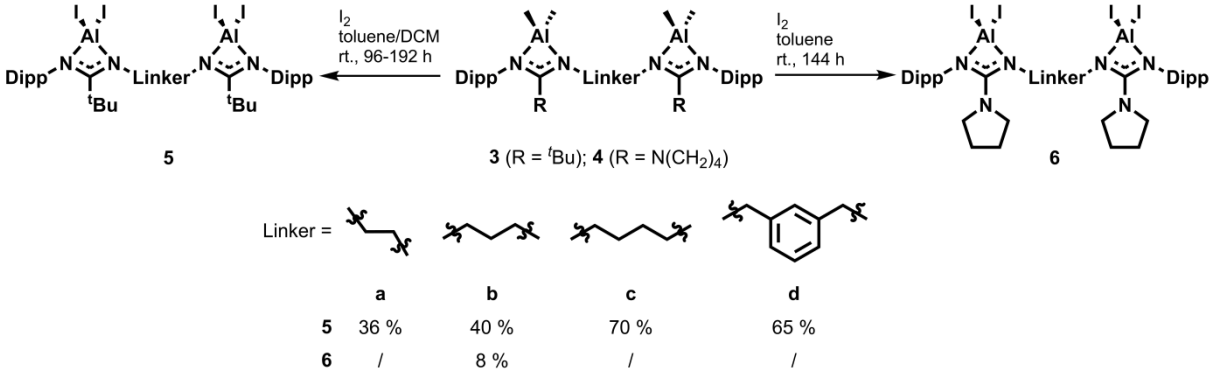


Figure 19. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) of a) **4a**, b) **4b**, and c) **4c**. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths (Å) and angles (°) of the dinuclear aluminium bis(guanidinate) complexes.

Compound	bond lengths			bond angles		
	Al–Al	Al–N	Al–R	N–Al–N	N–C–N	R–Al–R
4a	6.3264(9)	1.9203(11)-1.9339(11)	1.9653(14)-1.9651(16)	69.54(5)	108.8(1)	118.19(7)
4b	6.5520(6)	1.9196(13)-1.9271(13)	1.9553(17)-1.9692(16)	69.89(5)	108.64(11)-109.03(11)	117.11(7)-117.70(7)
4c	8.2085(6)	1.919(1)-1.929(1)	1.9561(14)-1.9645(14)	69.69(4)	108.94(10)	116.17(6)
6b	6.5975(10)	1.8703(16)-1.8757(2)	2.5027(6)-2.5076(6)	72.21(7)	108.19(15)	110.16(2)

Due to our interest in Group 13 analogues of bis(carbene)s[13] 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 ligand framework with methyl iodide formed during the reaction may account for this.



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

Besides the absence of the $Al(CH_3)_2$ resonances, the room-temperature ^1H NMR spectra resemble by and large those of the 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,[14] ^{27}Al NMR resonances could not been detected. In addition to the full characterization by elemental analyses, ^1H and ^{13}C 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 Figure 4 and 5a.

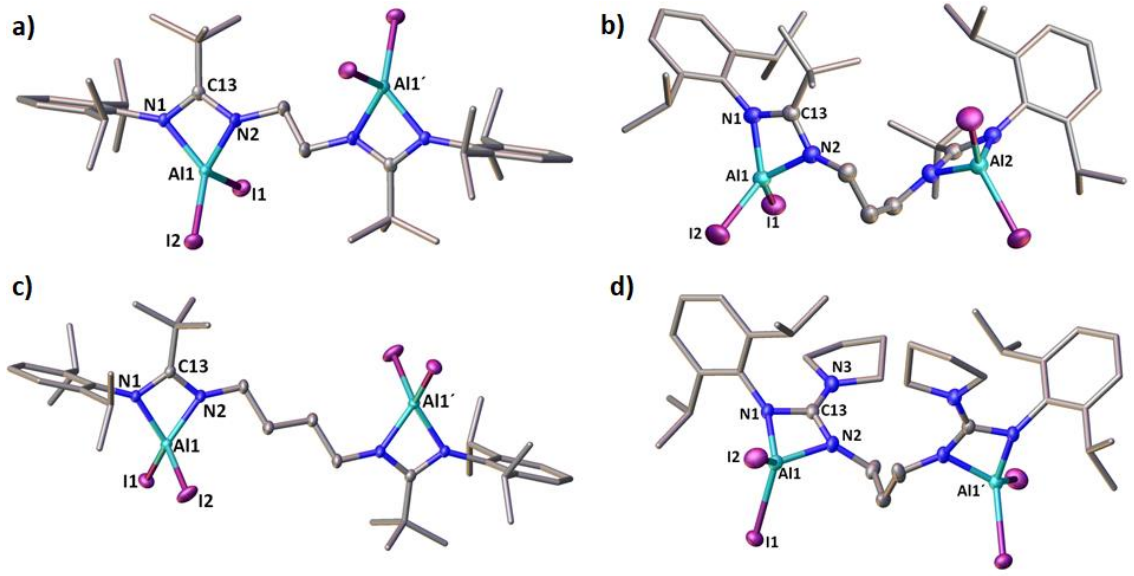
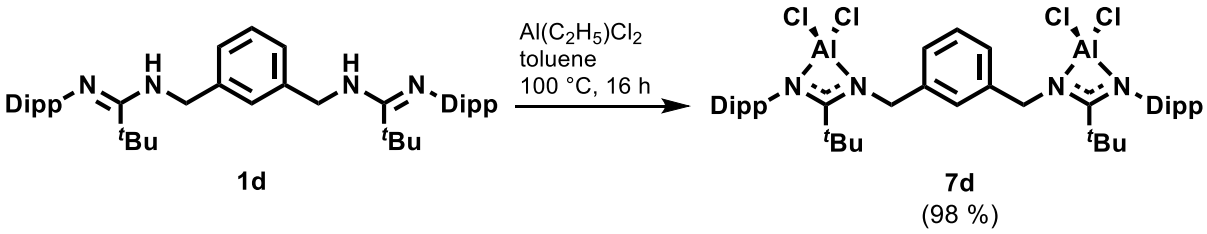


Figure 20. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) of a) **5a**, b) **5b**, c) **5c**, and d) **6b**. Selected bond lengths and angles are given in Table 1 and 2.

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).[15] 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),[16] 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).[12] 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 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**, Table 1 and 2. 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.



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

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 Figure 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 °).[10a] The Al–Al distance amounts to 7.4043(5) Å and is thus about 0.5 Å longer compared to **5d**.

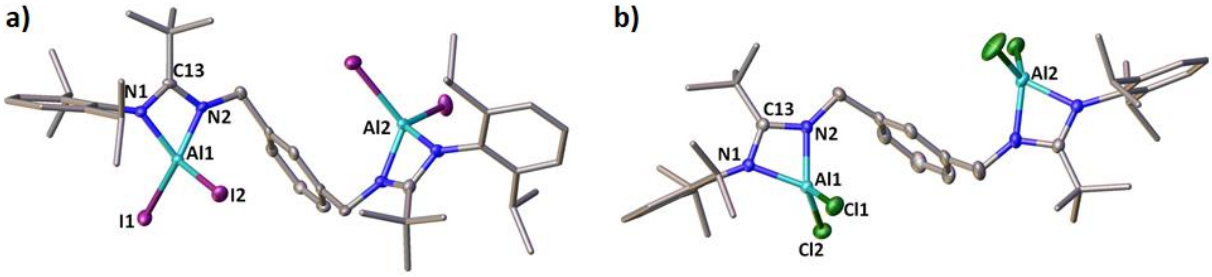


Figure 21. Solid-state structure (hydrogen atoms are omitted for the sake of clarity) of a) **5d** and b) **7d**. Selected bond lengths and angles are given in Table 1.

Attempts to obtain dinuclear aluminium(I) complexes by reducing the dinuclear complexes **5c**, **5d** and **7d** using either magnesium powder, cobaltocene or potassium mirror remained unsuccessful. As very low reduction potential have been reported for dinuclear aluminium bis(β-diketiminate) halide complexes,[14] 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 [{CH(CMeNDipp)$_2$}AlI$_2$] (-3.16 V),[14] were observed for the bis(amidinate) complexes, Figure S2-S7. 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 explains 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 *rac*-lactide and ε-caprolacton. While alcohols are regularly used as activators of dinuclear alkylaluminium complexes,[[6f,6g,6j] previous reports on dialkyl aluminium amidinate complexes mention a rapid alcoholysis.[10b] Hence, we first probed the stability of the four-membered $AlCN_2$-metallacycles towards protonolysis. Adding one or two equivalents of benzyl alcohol to the complexes **3b** and **4b**, respectively, Figure 6, affords the related protio-ligands along with other species most likely dimethyl aluminium benzylate according to the ^{1}H NMR shifts.[17] In consequence, and in agreement with previous reports on dialkyl aluminium amidinate complexes,[10b] mononuclear complexes are 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.

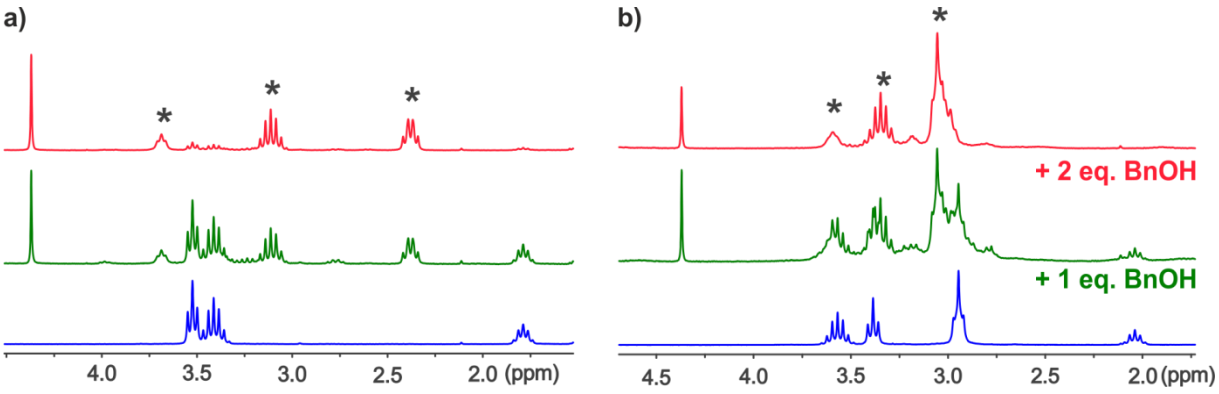


Figure 22. Excerpts of the ^{1}H NMR spectra of a) **3b** and b) **4b** in C_6D_6 before (blue) and after the addition of one (green) and two (red) equivalents of benzyl alcohol, respectively. Signals marked with an asterisk belong to the protio-ligands **1b** and **2b**, respectively.

In previous reports, dinuclear aluminium alkyl amidinate complexes have been successfully applied for the ROP of ε-caprolacton and *L*-lactide with and without the addition of an activator under various conditions.[6h] Aiming to test the catalytic performance of the complexes **3** and **4**, we adopted the experimental conditions and the results for ε-caprolacton and *L*-lactide are subsequently discussed in the following. ε-caprolacton 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 3. Polycaprolacton (PCL) was isolated with yields ranging from 75 to 90 % and better yields are associated with the bis(amidinate)s **3** in direct comparison with their bis(guanidinate) relatives **4**. The size-exclusion chromatography (SEC) traces, Figure S8-S15, possess multimodal distributions showing predominantly polymeric but also oligomeric products. A number average molar mass M_n between 17.000 and 23.400 Da and rather large polydispersities $Đ$ 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.

Table 3. ROP of ε-caprolacton 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	Yield (%)	M_n SEC (g mol^{-1})	Đ SEC (M_w/M_n)	Entry	Cat	Yield (%)	M_n SEC (g mol^{-1})	Đ SEC (M_w/M_n)
1	**3a**	82	2.27×10^4	2.34	5	**4a**	78	1.81×10^4	2.39
2	**3b**	90	2.29×10^4	2.20	6	**4b**	81	1.72×10^4	2.26
3	**3c**	89	4.37×10^4	2.07	7	**4c**	75	1.70×10^4	2.14
4	**3d**	88	2.69×10^4	2.30	8	**4d**	81	1.84×10^4	2.28

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 4. After 25 hours, the reactions were quenched and the products analysed by ^{1}H 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 are 1.6 to 1.8 times higher than the calculated values for one polymer chain per metal centre. Except the case of **3b**, the increased conversions at

90°C come along with larger polydispersity indices (PDIs) 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**. For both species, the butylene-bridged derivatives **3c** and **4c**, respectively, are associated with the highest PDI values, while the ethylene-bridged bis(amidinate) **3a** afforded the polymer with the narrowest polydispersity index (1.35).

Table 4. ROP of *L*-lactide catalysed by the dinuclear complexes **3** and **4**. Reaction conditions: toluene 1.5 mL, 25h, catalyst-monomer ratio = 1:200, [catalyst] = 1 x 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 (g mol^{-1})	Đ SEC (M_w/M_n)	Entry	Cat	Temp. (°C)	Conv.[a] (%)	Yield (%)	M_n calc[b] (g mol^{-1})	M_n SEC (g mol^{-1})	Đ SEC (M_w/M_n)
1	**3a**	80	35	25	5.04 x 10^3	5.27 x 10^3	1.18	9	**3a**	80	45	41	6.49 x 10^3	7.94 x 10^3	2.08
2	**3a**	90	83	83	1.20 x 10^4	1.35 x 10^4	1.35	10	**3a**	90	84	79	1.21 x 10^4	1.29 x 10^4	2.22
3	**3b**	80	35	29	5.04 x 10^3	8.09 x 10^3	1.66	11	**3b**	80	40	35	5.77 x 10^3	1.02 x 10^4	1.48
4	**3b**	90	92	88	1.33 x 10^4	1.78 x 10^4	1.58	12	**3b**	90	83	80	1.20 x 10^4	2.12 x 10^4	2.15
5	**3c**	80	39	35	5.62 x 10^3	9.02 x 10^3	1.43	13	**3c**	80	48	37	6.92 x 10^3	8.61 x 10^3	1.53
6	**3c**	90	90	88	1.30 x 10^4	1.41 x 10^4	1.80	14	**3c**	90	86	80	1.24 x 10^4	1.33 x 10^4	2.31
7	**3d**	80	36	24	5.19 x 10^3	4.94 x 10^3	1.17	15	**3d**	80	24	11	3.46 x 10^3	8.49 x 10^3	1.35
8	**3d**	90	86	83	1.24 x 10^4	9.34 x 10^3	1.59	16	**3d**	90	68	62	9.80 x 10^3	1.43 x 10^4	2.17

a) Determined by ^{1}H NMR spectroscopy, b) Calculated M_n = [monomer/Al] x (conversion/100) x MW *L*-lactide.

5.3 Conclusion

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 yields and more narrow polydispersity indices of both PCL and PLLA were observed using the former.

5.4 References

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5.5 Supporting information

General

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 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally P_4O_{10}. Dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS-800). Benzene-d_6 and toluene were used as 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**)[S1] as well as the bis(guanidines) (**2a**, **2b**, **2c**, **2d**)[S1,S2,S3] were prepared according to published procedures. Further information are given in the supplementary information.

Characterization. The NMR spectra were recorded with Bruker Avance 300 and 400 spectrometers (T = 300 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 ($CHCl_3$: δ(^{1}H) = 7.26) or (C_6D_6: δ(^{1}H) = 7.16) and the solvent peak ($CDCl_3$: δ(^{13}C) = 77.16) or (C_6D_6: δ(^{13}C) = 128.06), respectively. ^{27}Al NMR spectra were calibrated relative to external $Al(NO_3)_3 \cdot 9H_2O$. 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 ^{1}H NMR spectroscopy.

Protio-ligand synthesis

***Synthesis of N,N'*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide):**

A solution of pivaloylchloride (14.5 g, 120 mmol) in dichloromethane (30 mL) was added dropwise to a solution of 1,3(aminomethyl)benzylamine (8.16 g, 60.0 mmol) and trimethylamine (12.1 g, 120 mmol) in dichloromethane (400 mL). After stirring for three days at room temperature and 5 h under reflux, water (200 mL) was added to the white suspension giving a colorless biphasic solution. The organic phase was separated and washed with water (200 mL) and brine (200 mL). The product was dried over Na_2SO_4 and the solvent was removed yielding *N,N'*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) (17.5 g, 57.0 mmol, 96%) in analytically pure form as a white crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.19 (s, 18 H, $C(CH_3)_3$), 4.35 (d, 65.7 Hz, 4 H, $(C_6H_4)(CH_2)_2$), 6.13 (s, 2 H, N*H*), 7.09 (d, *J* = 7.5 Hz, 2 H, $CHC_2(CH)_2CH$), 7.12(s, 1 H, $CHC_2(CH)_2CH$) 7.24 (t, *J* = 7.5 Hz, 1 H, $CHC_2(CH)_2CH$). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.7 ($C(CH_3)_3$), 38.7 ($C(CH_3)_3$), 43.4 ($NCH_2C_6H_4$), 126.5 (*m*-C_6H_4), 126.7 (*o*-C_6H_4), 129.1 (*o*-C_6H_4), 139.3 (*i*-C_6H_4), 178.5 ($(CH_3)_3CC(O)NH$).

Synthesis of (1Z,1'Z)-N',N''-(1,3-phenylenebis(methylene))bis(2,2- dimethylpro-panimidoyl chloride):

Phosphorus pentachloride (23.9 g, 114 mmol) was added portionwise to a stirred solution of *N,N'*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) (17.5 g, 57.3 mmol) in toluene (300 mL). The reaction mixture was stirred at 100 °C for two days giving a yellow solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) (14.4 g, 42.0 mmol, 74 %) in analytically pure form as a dark brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.35 (s, 18 H, C(CH_3)$_3$), 4.73 (d, *J* = 4.8 Hz, 4 H, (CH_2)$_2$$C_6H_4$), 7.19-7.41 (m, 4H, C_6H_4). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 28.5 (C(CH_3)$_3$), 43.9 (*C*(CH_3)$_3$), 56.7 (N*C*$H_2C_6H_4$), 126.0 (*m*-C_6H_4), 127.5 (*o*-C_6H_4), 128.5 (*o*-C_6H_4), 138.8 (*i*-C_6H_4), 153.7 ((CH_3)$_3$C*C*(Cl)N).

Sythesis of (1Z,1'Z)-N',N''-(1,3-phenylenebis(methylene))bis(N-(2,6-diisopropyl-phenyl)- 2,2-dimethylpropanimidamide) (1d):

A solution of 2,6-diisopropylaniline (14.9 g, 84.2 mmol) in toluene (40 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) (14.4 g, 42.1 mmol) in toluene (160 mL). The reaction mixture was refluxed for three days giving a pale brown suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving a pale brown waxy solid. The raw product was suspended in ethylacetate (1000 mL) and stirred with a saturated sodium carbonate solution (1200 mL) over 1h giving a clear brown organic phase. The organic phase was separated and dried over sodium sulfate. The solvent was removed giving at first a brown oil that turned into a brown waxy solid after 16 h. The product was recrystallized from MeCN yielding **1d** (12.3 g, 19.7 mmol, 47 %) in analytically pure form as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.19 (d, *J* = 6.9 Hz, 12 H, $CH(CH_3)_2$), 1.20 (d, *J* = 6.9 Hz, 12 H, $CH(CH_3)_2$), 1.34 (s, 18 H, $C(CH_3)_3$), 3.03 (sept, *J* = 6.9 Hz, 4 H $CHCH_3)_2$), 3.73 (d, *J* = 5.1 Hz, 4 H, $(CH_2)_2C_6H_4$), 6.69-7.21 (m, 10H, C_6H_4 + C_6H_3). ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.5 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 28.5 ($C(CH_3)_3$), 29.3 ($CH(CH_3)_2$), 38.8 ($C(CH_3)_3$), 47.8 ($CH_2(C_6H_4)CH_2$), 121.1 (*m*-C_6H_3), 122.0 (*p*-C_6H_3), 126.7 (*m*-C_6H_4), 126.9 (*o*-C_6H_4), 129.1 (*o*-C_6H_4), 137.3 (*o*-C_6H_3), 139.6 (*i*-C_6H_4), 146.2 (*i*-C_6H_3), 156.4 ($NC(C(CH_3)_3)N$). IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3442 (w), 2958 (m), 2866 (w), 1653 (s), 1429 (m), 777 (m), 754 (m), 694 (m). HR MS (ESI-TOF): [M + H]+ for m/z $C_{42}H_{62}N_4$ 623.5052, found 623.5032.

Complex synthesis

Synthesis of 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 x 10 mL) to obtain **3a** (2.22 g, 3.37 mmol, 92 %) as a white crystalline solid.

^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = -0.21 (s, 12 H, $Al(CH_3)_2$), 1.05 (s, 18 H, $C(CH_3)_3$,), 1.22 – 1.25 (m, 24 H, $CH(CH_3)_2$), 3.41 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 3.86 (s, 4 H, CH_2CH_2), 7.00 – 7.10 (m, 6 H, C_6H_3); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): *δ (ppm)* = -9.1 ($Al(CH_3)_2$), 23.4 ($CH(CH_3)_2$), 26.3 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 28.5 ($C(CH_3)_3$), 40.0 ($C(CH_3)_3$), 48.9 (CH_2CH_2), 123.8 (*m*-C_6H_3), 125.9 (*p*-C_6H_3), 140.0 (*o*-C_6H_3), 144.3 (*i*-C_6H_3), 180.4 ($NC(C(CH_3)_3)N$); ^{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 [$C_{40}H_{68}N_4Al_2$]: C 73.76 (73.47), H 10.32 (10.02), N 8.11 (8.35).

Synthesis of 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 x 10 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.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = -0.66 (s, 12 H, $Al(CH_3)_2$), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.17(s, 18 H, $C(CH_3)_3$,), 1.27 (d, $^3J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.84 (quint, $^3J_{HH}$ = 6.3 Hz, 2 H, $CH_2(CH_2)CH_2$), 3.25 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 3.65 (t, $^3J_{HH}$ = 6.4 Hz, 4 H, $CH_2(CH_2)CH_2$), 7.04 – 7.13 (m, 6 H, C_6H_3; $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -9.7 ($Al(CH_3)_2$), 23.3 ($CH(CH_3)_2$), 26.2 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 28.7 ($C(CH_3)_3$), 34.1 ($CH_2(CH_2)CH_2$), 39.9 ($C(CH_3)_3$), 43.5 ($CH_2(CH_2)CH_2$), 123.4 (*m*-C_6H_3), 125.0 (*p*-C_6H_3), 140.2 (*o*-C_6H_3), 144.2 (*i*-C_6H_3), 180.2 ($NC(C(CH_3)_3)N$); ^{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 [$C_{41}H_{70}N_4Al_2$]: C 73.43 (73.39), H 10.56 (10.55), N 8.16 (8.26).

Synthesis of 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 1h. After solvent filtration the white crystalline powder was washed with toluene (2 x 5 mL) to afford **3c** (1.04 g, 1.5 mmol, 75 %) as a white crystalline powder.

^{1}H NMR (300 MHz, $CDCl_3$): *δ(ppm)* = -0.69 (s, 12 H, $Al(CH_3)_2$), 1.12 – 1.16 (m, 30 H, $C(CH_3)_3$, $CH(CH_3)_2$), 1.26 – 1.29 (m, 12 H, $CH(CH_3)_2$), 1.66 (quint, $^3J_{HH}$ = 3.3 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 3.27 (sept, $^3J_{HH}$ = 6.9 Hz, 4 H, $CH(CH_3)_2$), 3.53 (t, $^3J_{HH}$ = 6.0 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 7.03 – 7.20 (m, 6 H, C_6H_3); $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -9.7 ($Al(CH_3)_2$), 23.4 ($CH(CH_3)_2$, 26.2 ($CH(CH_3)_2$), 28.0 ($C(CH_3)_3$), 28.8 ($CH(CH_3)_2$, 30.2 ($C(CH_3)_3$), 39.8 ($CH_2(CH_2)_2CH_2$), 46.6 ($CH_2(CH_2)_2CH_2$), 123.4 (*m*-C_6H_3), 125.0 (*p*-C_6H_3), 140.3 (*o*-C_6H_3), 144.4 (*i*-C_6H_3), 179.6 ($NC(C(CH_3)_3)N$); ^{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 [$C_{42}H_{72}N_4Al_2$]: C 73.17 (73.38), H 10.48 (10.25), N 8.33 (8.09).

Synthesis of 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. ^{1}H NMR (400 MHz, C_6D_6): *δ(ppm)* = -0.74 (s, 12 H, $Al(CH_3)_2$), 1.32 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$), 1.41 (s, 18 H, $C(CH_3)_3$), 1.48 (d, $^3J_{HH}$ = 6.9 Hz, 12 H, $CH(CH_3)_2$), 3.49 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 4.90 (s, 4 H, $CH_2C_6H_4CH_2$), 7.23 – 7.60 (m, 10 H, C_6H_3 + C_6H_4); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): *δ (ppm)* = -9.4 ($Al(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 26.4 ($CH(CH_3)_2$), 28.2 ($C(CH_3)_3$), 28.8 ($CH(CH_3)_2$), 39.8 ($C(CH_3)_3$), 51.2 ($CH_2C_6H_4CH_2$), 123.8 (*m*-C_6H_3), 125.8 (*p*-C_6H_3), 127.7 (*m*-C_6H_4), 128.7 (*o*-C_6H_4), 129.4 (*o*-C_6H_4), 140.3 (*o*-C_6H_3), 140.8 (*i*-C_6H_4), 144.3 (*i*-C_6H_3), 179.8 ($NC(C(CH_3)_3)N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed; IR (ATR): *ṽ* [cm^{-1}] = 2961 (m), 2921 (w), 2867 (w), 1413 (s), 1321 (s), 1184 (s), 669 (s); Anal. calc. (found) for [$C_{46}H_{72}N_4Al_2$]: C 75.16 (75.11), H 9.87 (9.65), N 7.62 (7.61).

Synthesis of 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.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = -0.72 (s, 12 H, $Al(CH_3)_2$), 1.13 (d, $^{3}J_{HH}$ = 6.8 Hz,12 H, $CH(CH_3)_2$), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz,12 H, $CH(CH_3)_2$), 1.71 – 1.74 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.09 – 3.14 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.33 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 3.44 (s, 4 H, CH_2CH_2), 7.04 – 7.10 (m, 6 H, C_6H_3); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -9.5 ($Al(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 25.7 ($N(CH_2)_2(CH_2)_2$), 25.9 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 47.5 (CH_2CH_2), 48.6 ($N(CH_2)_2(CH_2)_2$), 123.3 (*m*-C_6H_3), 124.5 (*p*-C_6H_3), 139.4 (*o*-C_6H_3), 144.9 (*i*-C_6H_3), 162.5 ($NC(N(CH_2)_2(CH_2)_2)_3N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed; IR (ATR): *ṽ* [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 [$C_{40}H_{66}N_6Al_2$]: C 70.14 (69.65), H 9.71 (9.23), N 12.27 (12.91).

Synthesis of 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.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = -0.72 (s, 12 H, $Al(CH_3)_2$), 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz,12 H, $CH(CH_3)_2$), 1.19 (d, $^{3}J_{HH}$ = 6.9 Hz,12 H, $CH(CH_3)_2$), 1.69 – 1.72 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 1.85 (qui, 2 H, $CH_2(CH_2)CH_2$, 3.08 – 3.11 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.30 – 3.37 (m, 8 H, $CH(CH_3)_2$)+

$CH_2(CH_2)CH_2$), 7.03 – 7.07 (m, 6 H, C_6H_3); $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -9.6 ($Al(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 25.7 ($N(CH_2)_2(CH_2)_2$), 25.9 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 33.4 ($CH_2(CH_2)CH_2$), 43.6 ($CH_2(CH_2)CH_2$), 48.6 ($N(CH_2)_2(CH_2)_2$), 123.2 (*m*-C_6H_3), 124.5 (*p*-C_6H_3), 139.5 (*o*-C_6H_3), 144.8 (*i*-C_6H_3), 162.7 ($NC(N(CH_2)_2(CH_2)_2)_3N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *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 [$C_{41}H_{68}N_6Al_2$]: C 70.45 (70.48), H 9.81 (9.54), N 12.02 (11.93).

Synthesis of 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, $CDCl_3$): *δ(ppm)* = -0.73 (s, 12 H, $Al(CH_3)_2$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz,12 H, $CH(CH_3)_2$), 1.18 (d, $^3J_{HH}$ = 6.9 Hz,12 H, $CH(CH_3)_2$), 1.62 – 1.67 (m, 8 H, $CH_2(CH_2)_2CH_2$), 1.69 – 1.72 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.08 – 3.11 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.23 – 3.26 (m, 4 H, $CH_2(CH_2)_2CH_2$), 3.33 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 7.03 – 7.09 (m, 6 H, C_6H_3); $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -9.5 ($Al(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 25.7 ($N(CH_2)_2(CH_2)_2$), 25.9 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 34.3 ($CH_2(CH_2)_2CH_2$), 46.2 ($CH_2(CH_2)_2CH_2$), 48.6 ($N(CH_2)_2(CH_2)_2$), 123.4 (*m*-C_6H_3), 124.4 (*p*-C_6H_3), 139.5 (*o*-C_6H_3), 144.8 (*i*-C_6H_3), 162.5 ($NC(N(CH_2)_2(CH_2)_2)_3N$);

^{27}Al NMR (104 MHz, $CDCl_3$): *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 [$C_{42}H_{70}N_6Al_2$]: C 70.75 (70.68), H 9.90 (9.43), N 11.79 (11.56).

Synthesis of 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 x 5 mL). Recrystallization in DCM at rt. overnight gave the product **4d** (2.16 g, 2.83 mmol, 92 %) as clear colorless crystals.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = -0.90 (s, 12 H, $Al(CH_3)_2$), 1.15 (d, $^3J_{HH}$ = 6.8 Hz,12 H, $CH(CH_3)_2$), 1.20 (d, $^3J_{HH}$ = 6.9 Hz,12 H, $CH(CH_3)_2$), 1.62 – 1.65 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.04 – 3.07 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.40 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 4.44 (s, 4 H, $CH_2(C_6H_4)CH_2$), 7.03 – 7.11 (m, 6 H, C_6H_3), 7.29 – 7.38 (m, 4 H, $CH_2(C_6H_4)CH_2$); $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = -10.3 ($Al(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 25.6 ($N(CH_2)_2(CH_2)_2$), 25.9 ($CH(CH_3)_2$), 27.7 ($CH(CH_3)_2$), 48.5 ($N(CH_2)_2(CH_2)_2$), 49.7 ($CH_2(C_6H_4)CH_2$) 123.3 (*m*-C_6H_3), 124.5 (*p*-C_6H_3), 125.5 (*o*-C_6H_4), 126.1 (*o*-C_6H_4), 128.8 (*m*-C_6H_4), 139.5 (*o*-C_6H_3),141.9 (*i*-C_6H_4), 144.8 (*i*-C_6H_3), 162.8 ($NC(N(CH_2)_2(CH_2)_2)_3N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *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 [$C_{46}H_{70}N_6Al_2$]: C 72.60 (72.30), H 9.27 (8.86), N 11.04 (10.72).

Synthesis of 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 x 10 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with pentane (5 x 10 mL). A second crop of crystals was obtained by concentration of the mother solution, crystallization and washing with pentane (7 x 10 mL). **5a** (724 mg, 0.66 mmol, 36 %) was obtained as a pale brown crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.25 (s, 18 H, $C(CH_3)_3$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.30 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 3.30 (sept, $^3J_{HH}$ = 6.7 Hz, 4 H, $CH(CH_3)_2$), 4.05 (s, 4 H, CH_2CH_2), 7.11 – 7.23 (m, 6 H, C_6H_3); $^{13}C\{^1H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.6 ($CH(CH_3)_2$), 28.1 ($CH(CH_3)_2$), 28.3 ($C(CH_3)_3$), 40.4 ($C(CH_3)_3$), 47.1 (CH_2CH_2), 124.2 (*m*-C_6H_3), 127.1 (*p*-C_6H_3), 136.4 (*o*-C_6H_3), 144.8 (*i*-C_6H_3), 185.7 ($NC(C(CH_3)_3)N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed. A small signal at −24.7 ppm was observed, which account for the formation of $[AlI_4]^-$ and might be caused by slow degradation; IR (ATR): *ṽ* [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 [$C_{36}H_{56}N_4Al_2I_2$]: C 39.08 (39.10), H 5.10 (5.15), N 5.06 (4.90).

Synthesis of 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 x 10 mL) to afford **5b** (1.80 g, 1.6 mmol, 40 %) as pale brown crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.23 (s, 18 H, $C(CH_3)_3$), 1.25 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.28 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 2.20 (quint, $^{3}J_{HH}$ = 5.9 Hz, 2 H, $CH_2(CH_2)CH_2$), 3.28 (sept, $^{3}J_{HH}$ = 6.7 Hz, 4 H, $CH(CH_3)_2$), 3.90 (t, $^{3}J_{HH}$ = 5.9 Hz, 4 H, $CH_2(CH_2)CH_2$), 7.09 – 7.22 (m, 6 H, C_6H_3); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.6 ($C(CH_3)_3$), 28.2 ($CH(CH_3)_2$), 28.3 ($C(CH_3)_3$), 31.5 ($CH_2(CH_2)CH_2$), 40.4 ($C(CH_3)_3$), 43.7 ($CH_2(CH_2)_2CH_2$), 124.1 (*m*-C_6H_3), 127.0 (*p*-C_6H_3), 136.6 (*o*-C_6H_3), 144.7 (*i*-C_6H_3), 186.1 ($NC(C(CH_3)_3)N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed. A small signal at −24.8 ppm was observed, which account for the formation of $[AlI_4]^-$ 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 [$C_{42}H_{72}N_4Al_2 \cdot 0.4$ DCM]: C 38.91 (38.96), H 5.13 (5.14), N 4.85 (4.73).

Synthesis of 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 x 10 mL) to afford **5c** (3.16 g, 2.8 mmol, 70 %) as pale brown crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.20 (s, 18 H, $C(CH_3)_3$), 1.26 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.31 (d, $^{3}J_{HH}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.95 (quint, $^{3}J_{HH}$ = 3.3 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 3.32 (sept, $^{3}J_{HH}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$), 3.67 (t, $^{3}J_{HH}$ = 6.0 Hz, 4 H, $CH_2(CH_2)_2CH_2$), 7.09 – 7.21 (m, 6 H, C_6H_3); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.7 ($C(CH_3)_3$), 28.2 ($CH(CH_3)_2$), 28.2 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 29.4 ($CH_2(CH_2)_2CH_2$), 40.3 ($C(CH_3)_3$), 46.5 ($CH_2(CH_2)_2CH_2$), 124.1 (*m*-C_6H_3), 126.9 (*p*-C_6H_3), 136.8 (*o*-C_6H_3), 145.0 (*i*-C_6H_3), 185.2 ($NC(C(CH_3)_3)N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed. A small signal at −24.7 ppm was observed, which account for the formation of $[AlI_4]^-$ 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 [$C_{42}H_{72}N_4Al_2 \cdot 0.8$ DCM]: C 38.76 (38.57), H 5.16 (5.35), N 4.66 (4.56).

Synthesis of 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 x 40 mL). Solvent removal and recrystallization from DCM gave brownish crystals which were further washed with pentane (5 x 10 mL). A

second crop of crystals was obtained by concentration of the mother solution, crystallization and washing with pentane (7 x 10 mL). **5d** (6.17 g, 5.2 mmol, 65 %) was obtained as a pale brown crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.26 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.29 (s, 18 H, C(CH$_3$)$_3$), 1.33 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, C*H*(CH$_3$)$_2$), 3.36 (sept, $^{3}J_{HH}$ = 6.7 Hz, 4 H, CH(CH$_3$)$_2$), 4.83 (s, 4 H, $CH_2C_6H_4CH_2$), 7.10 – 7.70 (m, 10 H, C_6H_3 + C_6H_4); ^{13}C{^{1}H} NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.7 (C(CH$_3$)$_3$), 28.2 (CH(CH$_3$)$_2$), 28.3 (CH(CH$_3$)$_2$), 28.5 (CH(CH$_3$)$_2$), 40.3 (C(CH$_3$)$_3$), 50.6 ($CH_2C_6H_4CH_2$), 124.1 (*m*-C_6H_3), 126.9 (*p*-C_6H_3), 128.9 (*m*-C_6H_4), 126.6 (*o*-C_6H_4), 130.6 (*o*-C_6H_4), 136.7 (*o*-C_6H_3), 138.0 (*i*-C_6H_4), 144.8 (*i*-C_6H_3), 185.0 (NC(C(CH$_3$)$_3$)N); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed. A small signal at −24.6 ppm was observed, which account for the formation of $[AlI_4]^-$ and might be caused by slow degradation; IR (ATR): *ṽ* [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 $[C_{42}H_{60}N_4Al_2I_4]$: C 42.66 (42.32), H 5.11 (5.38), N 4.4.76 (4.30).

Synthesis of 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 x 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.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.21 (dd, $^{3}J_{HH}$ = 6.8 Hz,14 H, $CH(CH_3)_2$), 1.75 – 1.80 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 2.24 (qui, 2 H, $CH_2(CH_2)CH_2$), 3.00 – 3.29 (m, 8 H, $N(CH_2)_2(CH_2)_2$), 3.35 (sept, $^{3}J_{HH}$ = 6.9 Hz, 4 H, $CH(CH_3)_2$), 3.58 (t, $^{3}J_{HH}$ = 6.9 Hz, 4 H, $CH_2(CH_2)CH_2$), 7.08 – 7.19 (m, 6 H, C_6H_3); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.1 ($CH(CH_3)_2$), 25.6 ($N(CH_2)_2(CH_2)_2$), 27.4 ($CH(CH_3)_2$), 28.0 ($CH(CH_3)_2$), 32.3 ($CH_2(CH_2)CH_2$), 42.6 ($CH_2(CH_2)CH_2$), 49.7 ($N(CH_2)_2(CH_2)_2$), 123.9 (*m*-C_6H_3), 126.4 (*p*-C_6H_3), 136.0 (*o*-C_6H_3), 145.4 (*i*-C_6H_3), 163.9 ($NC(N(CH_2)_2(CH_2)_2)_3N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *δ (ppm)* = no signal observed. A small signal at −24.9 ppm was observed, which account for the formation of $[AlI_4]^-$ 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 [$C_{40}H_{66}N_6Al_2$]: Even after repeated attempts no suitable elemental analysis could be obtained.

Synthesis of 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.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.23 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 1.29 (s, 18 H, $C(CH_3)_3$), 1.32 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, $CH(CH_3)_2$), 3.26 (sept, $^{3}J_{HH}$ = 6.7 Hz, 4 H, $CH(CH_3)_2$), 4.78 (s, 4 H, $CH_2C_6H_4CH_2$), 7.09 – 7.57 (m, 10 H, C_6H_3 + C_6H_4); $^{13}C\{^{1}H\}$ NMR (101 MHz,$CDCl_3$): *δ (ppm)* = 23.5 ($C(CH_3)_3$), 26.3 ($CH(CH_3)_2$), 28.4 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 40.0 ($C(CH_3)_3$), 50.5 ($CH_2C_6H_4CH_2$), 123.9 (*m*-C_6H_3), 126.7 (*p*-C_6H_3), 128.0 (*m*-C_6H_4), 128.6 (*o*-C_6H_4), 129.8 (*o*-C_6H_4), 136.9 (*o*-C_6H_3), 139.0 (*i*-C_6H_4), 144.6 (*i*-C_6H_3), 185.7 ($NC(C(CH_3)_3)N$); ^{27}Al NMR (104 MHz, $CDCl_3$): *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 [$C_{42}H_{60}N_4Al_2I_4$]: 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 x 10^{-6} mol, 1 equiv., 0.007 mol L^{-1}), ε-aprolacton (0.3 mL, 30.3 x 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 x 5 mL) and dried in vacuum to a constant weight.

Ring-opening polymerization of *L*-lactide: In a glovebox, a glass vial equipped with a stir bar was charged with the catalyst 15.2 x 10^{-6} mol, 1 equiv., 0.01 mol L^{-1}), *L*-lactid (437 mg, 30.3 x 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 adding5 mL of ethanol. . The product was filtered off, washed with ethanol (2 x 5 mL) and dried in vacuum to a constant weight.

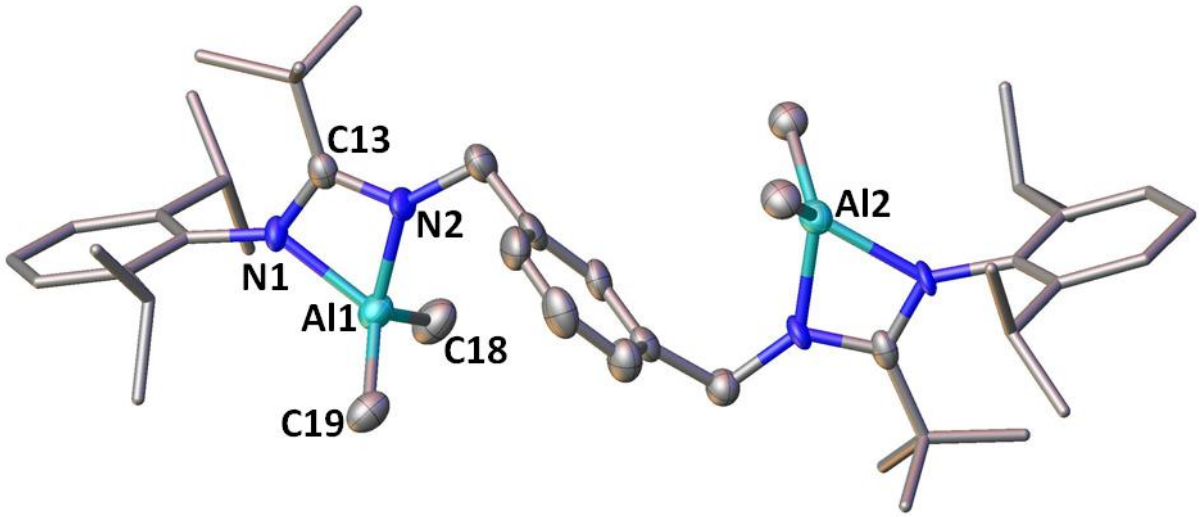

Figure S1 Motif of the solid state structure (hydrogen atoms are omitted for the sake of clarity) of **3d.**

Cyclic Voltammorgrams

All cyclic voltammetry measurements were performed in THF at 295 K using a three electrode setup, with a platinum disc electrode (working electrode, 3 mm diameter), a non-aqueous Ag/Ag+ electrode (pseudo-reference electrode) and a Pt-wire (auxiliary electrode), in combination with either a Potentiostat EmStat3+ by the company PalmSens, Compact Electrochemical Interfaces or *CHI 600E* Potentiostat by the company CH Instruments, Inc.. Bu_4NPF_6 (0.1 mol/L) was used as supporting electrolyte and all cyclic voltammograms are referenced against the Fc/Fc+ redox couple.

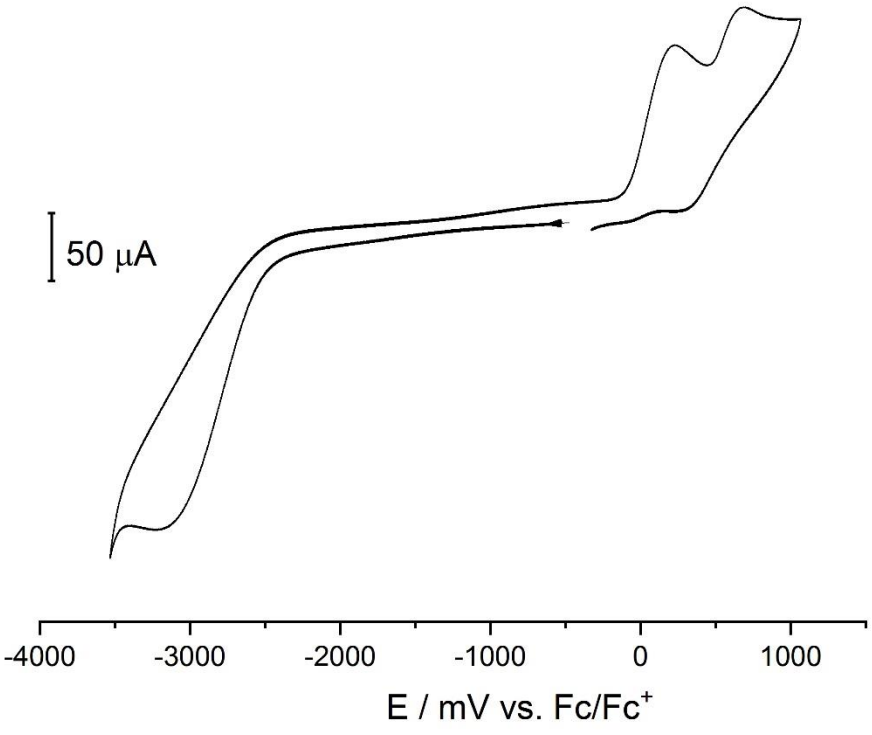

Figure S2 Cyclic voltammogram of **5a** vs. Fc/Fc+.

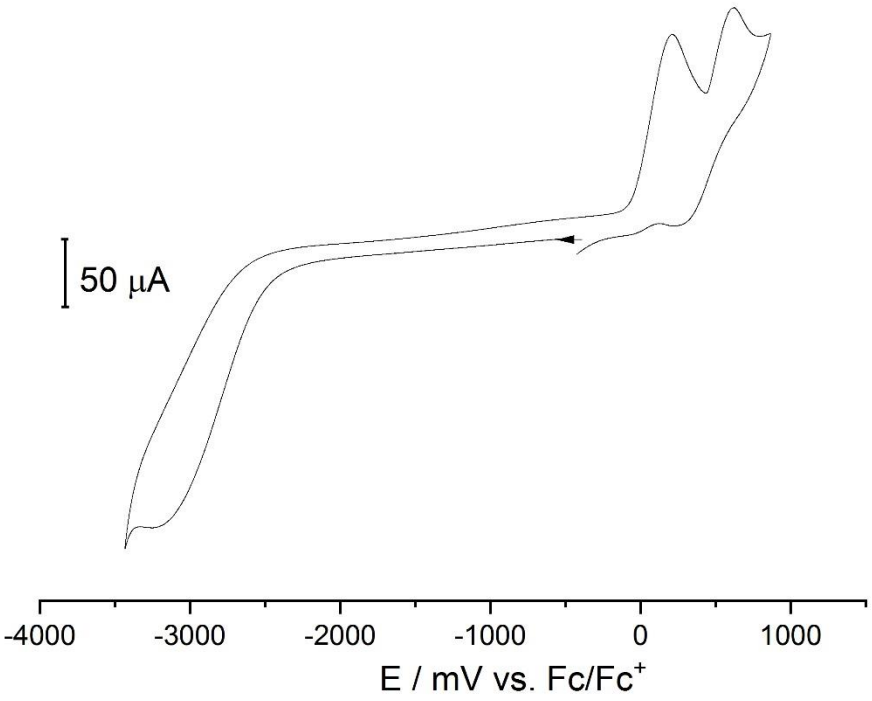

Figure S3 Cyclic voltammogram of **5b** vs. Fc/Fc+.

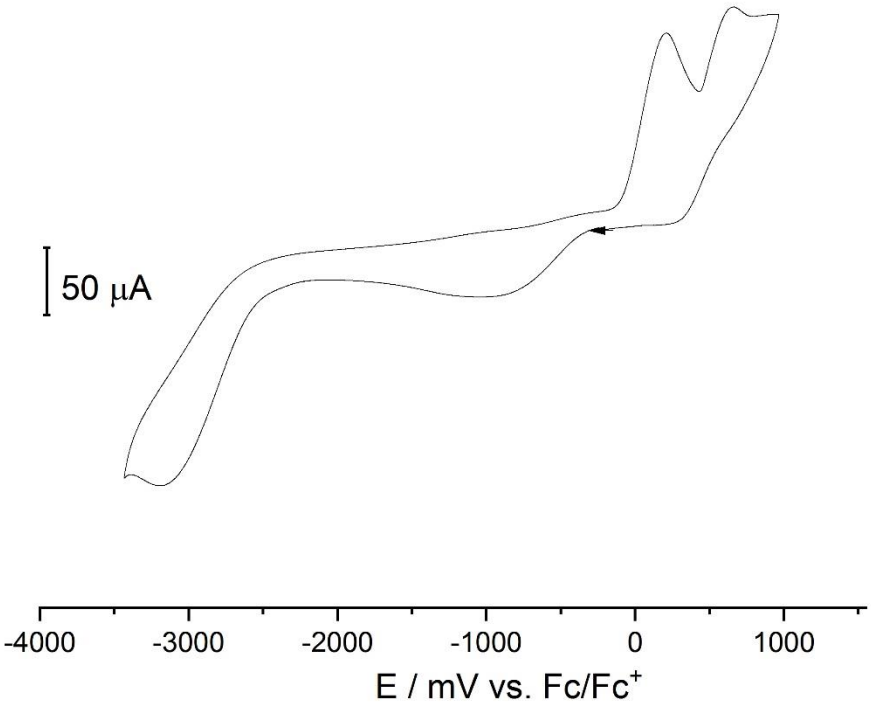

Figure S4 Cyclic voltammogram of **5c** vs. Fc/Fc+.

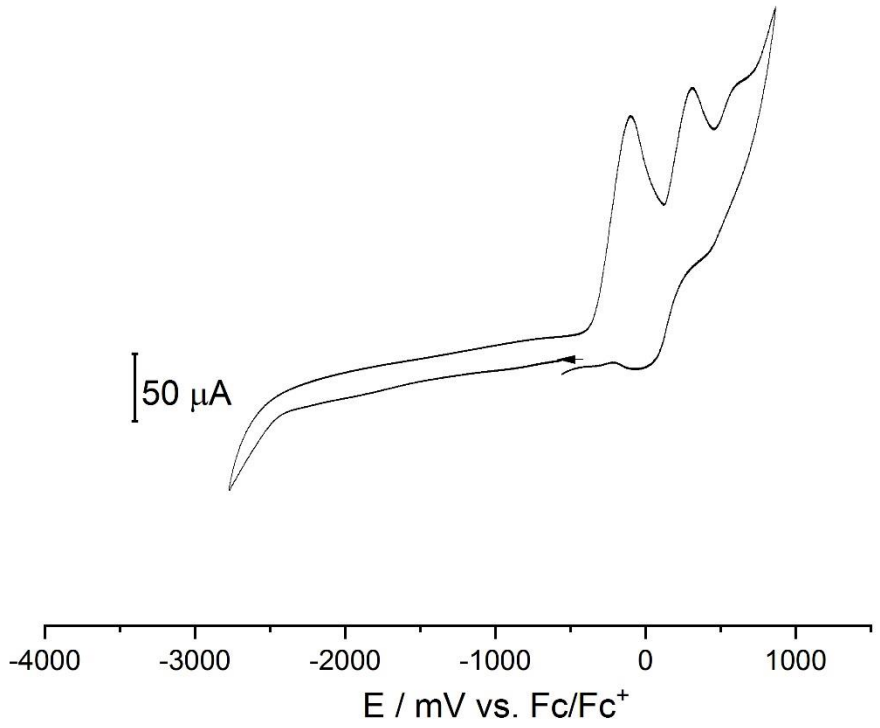

Figure S5 Cyclic voltammogram of **5d** vs. Fc/Fc+.

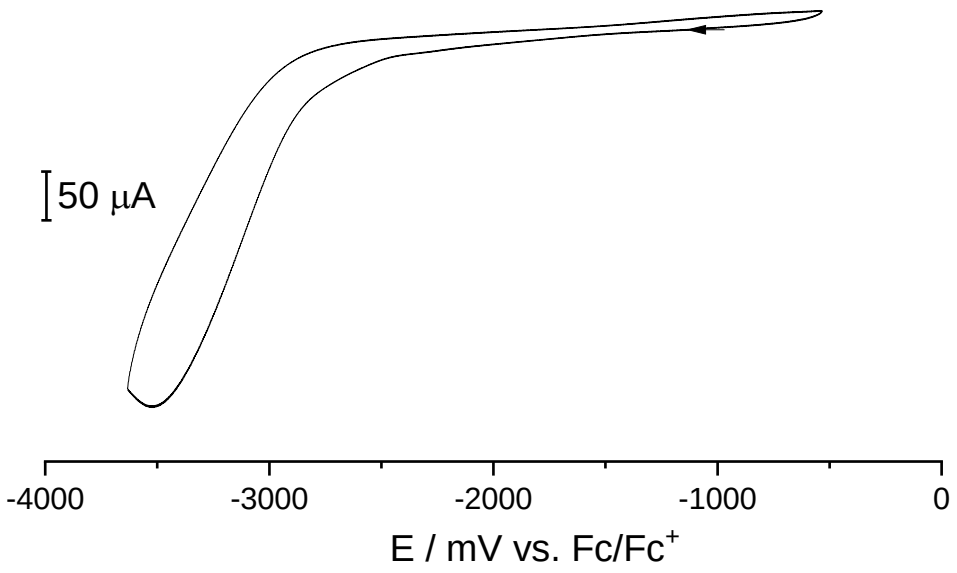

Figure S6 Negative run of the cyclic voltammogram of **5d** vs. Fc/Fc+.

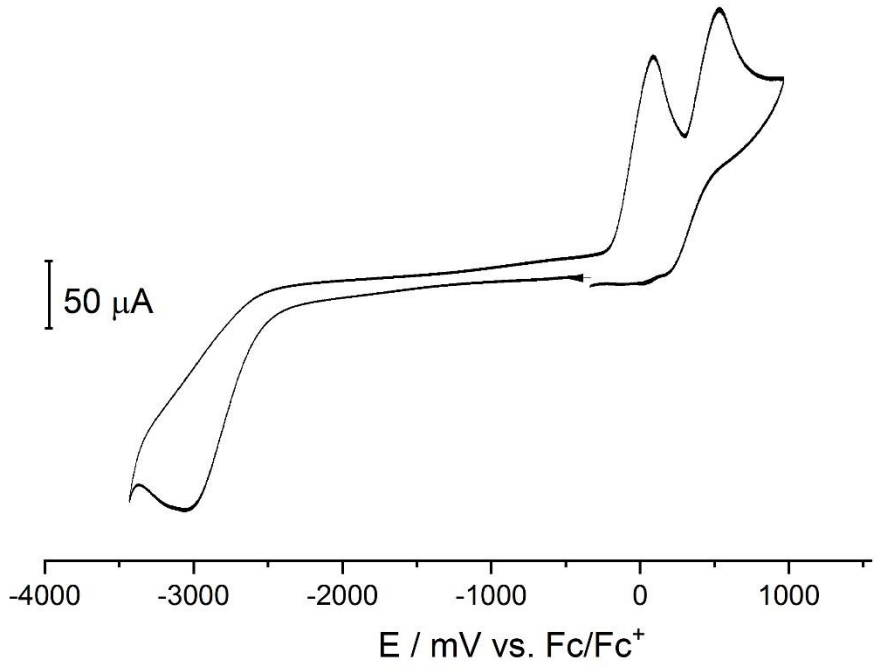

Figure S7 Cyclic voltammogram of **6b** vs. Fc/Fc+.

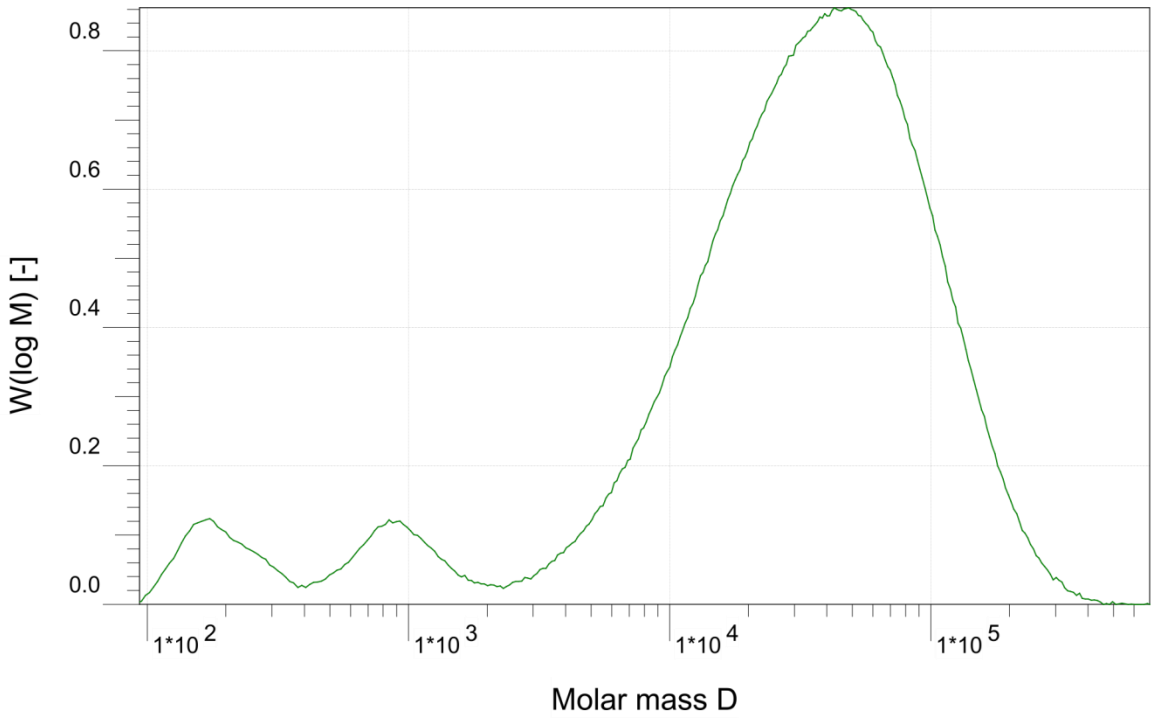

Figure S8 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3a.**

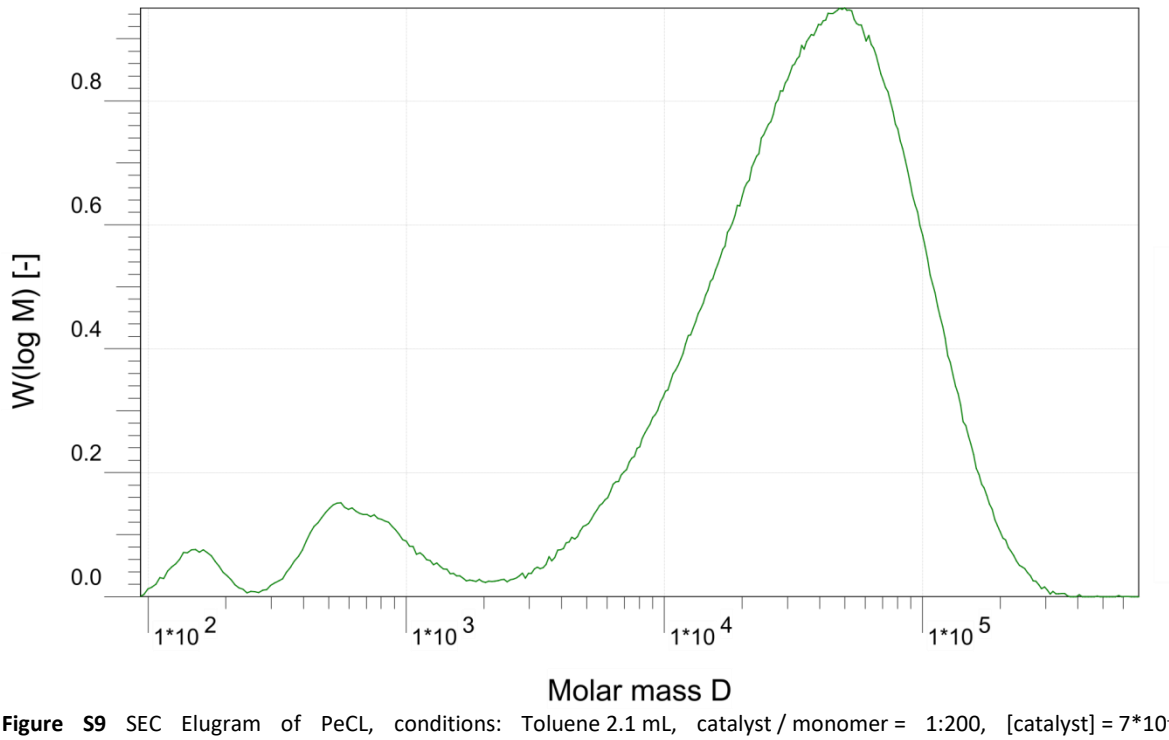

Figure S9 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3b.**

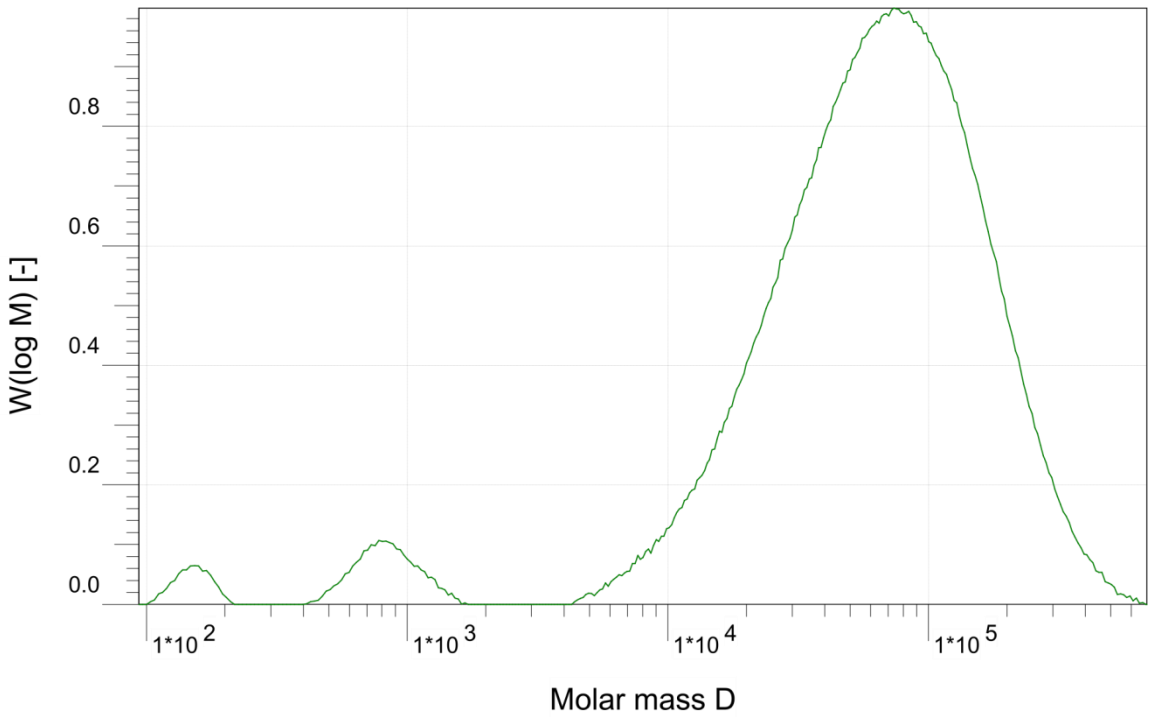

Figure S10 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3c**.

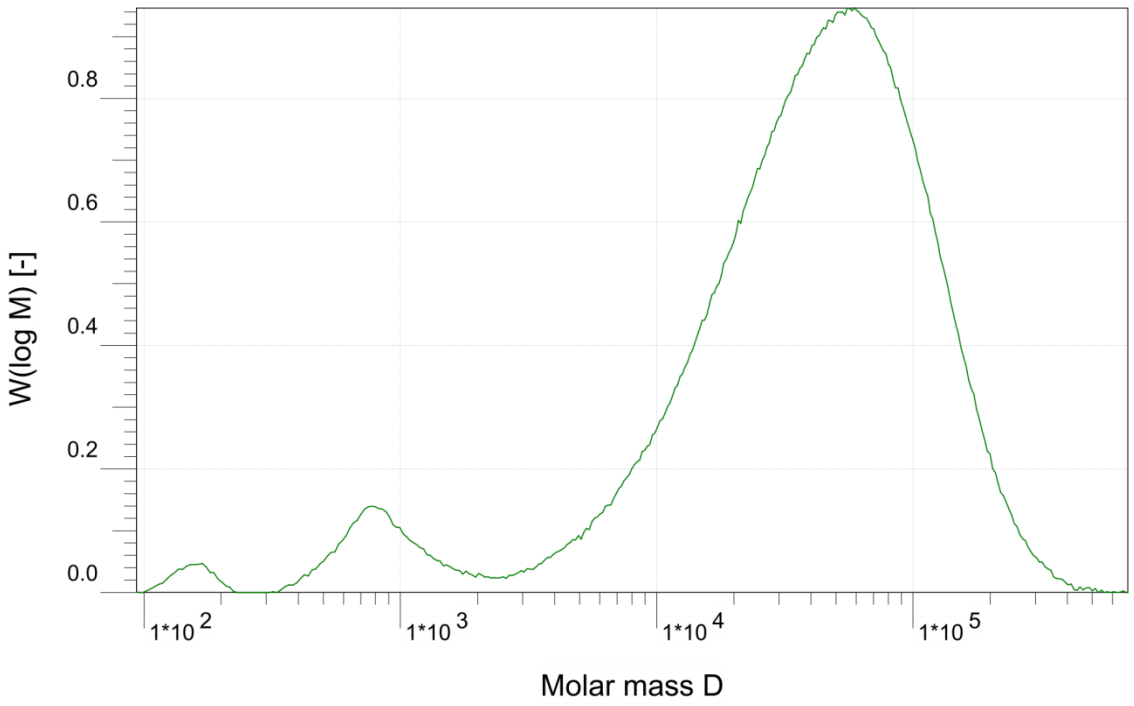

Figure S11 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3d**.

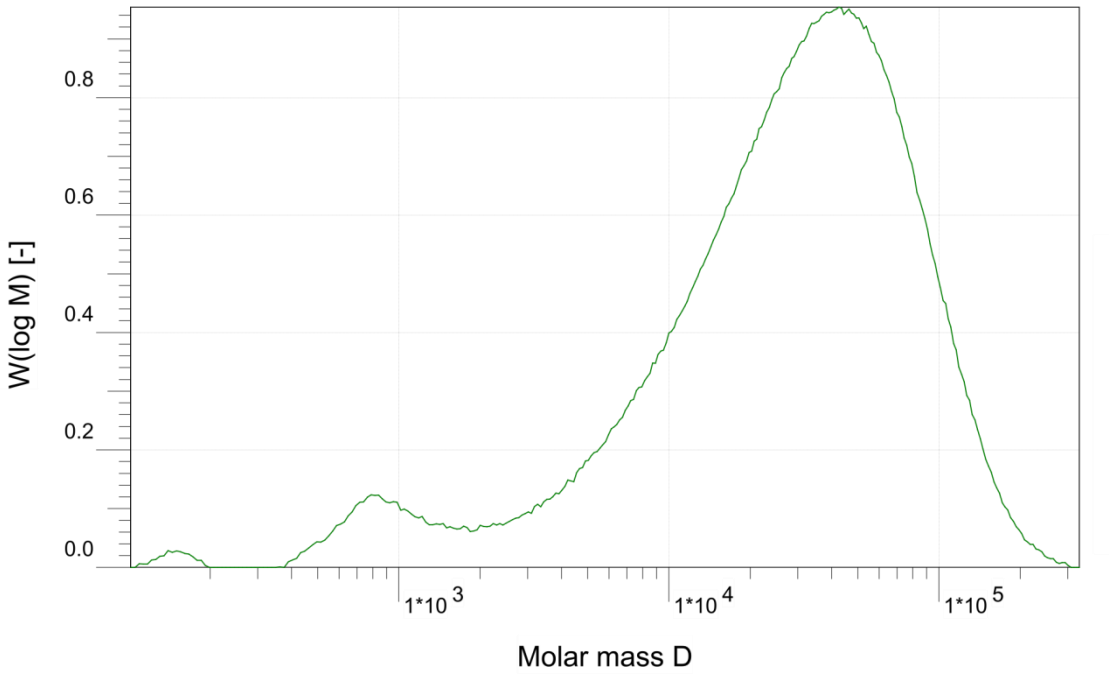

Figure S12 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4a**.

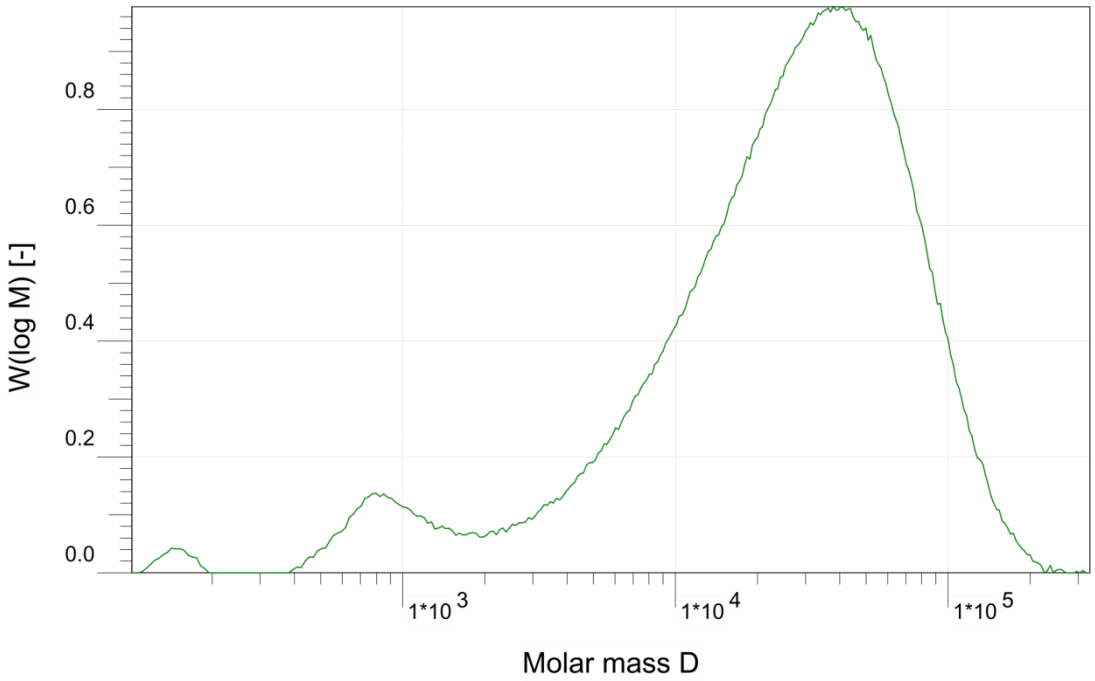

Figure S13 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4b**.

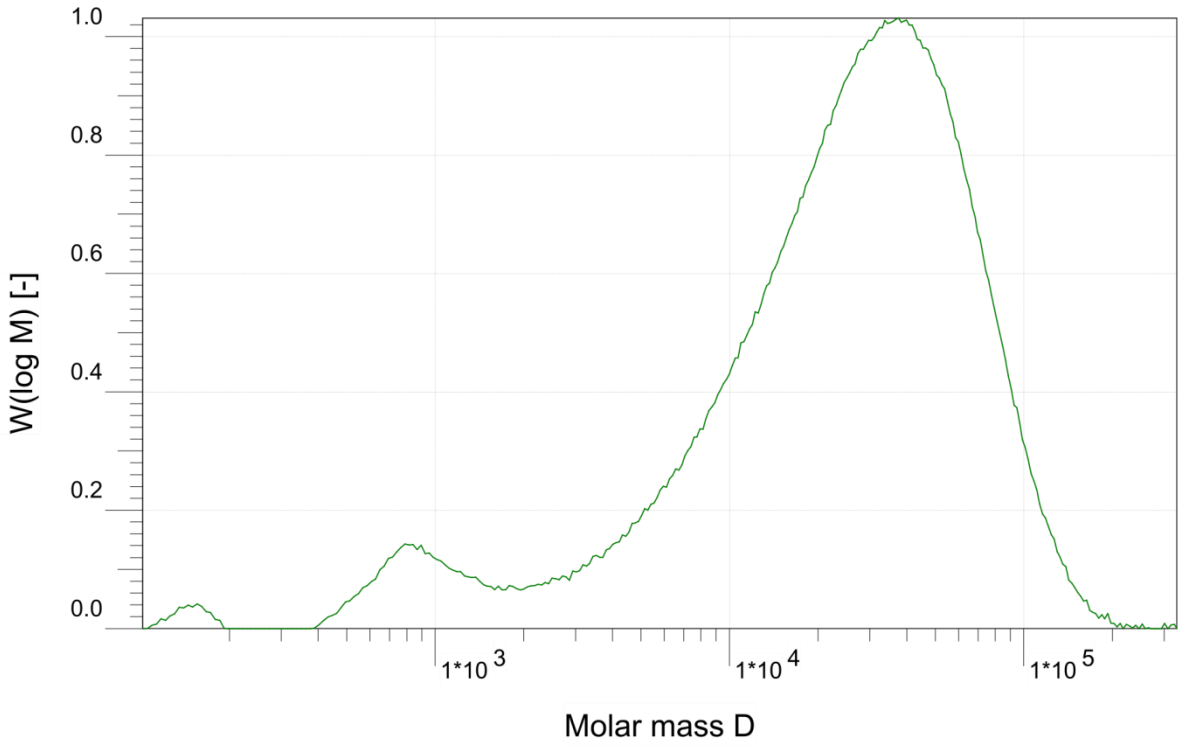

Figure S14 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4c.**

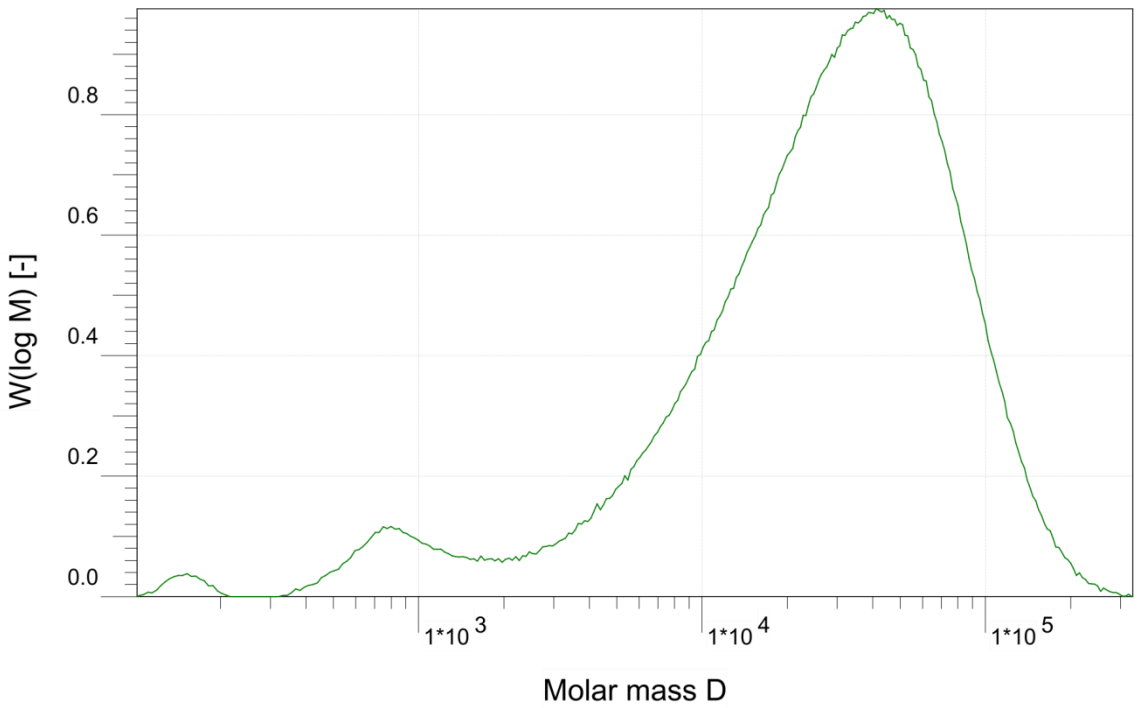

Figure S15 SEC Elugram of PeCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = $7*10^{-2}$ M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4d.**

Crystallographic details

The intensity data were collected on a GV-50 diffractometer with TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying a Mo Kα radiation (λ = 0.71073 Å fot compound **5d**), an Cu Kβ radiation (λ =1.39222 Å for compound **6b**), and an Cu Kα radiation (λ = 1.54184 Å for all other compounds). Data were corrected for Lorentz and polarization effects; an analytical absorption corrections were applied to the data.[S4] The structures were solved by direct methods (SHELXT)[S5] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-2018)[S6]. All hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystal of **5d** and **6b** contains large voids, filled with disordered solvent molecules. The size of the voids are 324 and 973 $Å^3$/unit cell, respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON[S7] resulting in 78 and 170 electrons/unit cell, respectively. Additional, the crystal of **5d** was a non-merohedral twin. The twin law was determined by PLATON[S7] to (-1.000 0.003 0.000) (0.000 1.000 0.000) (0.000 0.986 -1.000). The contribution of the main component were refined to 0.5015(7). All non-hydrogen atoms were refined anisotropically.[5] The crystals of **3d** were extremely thin and of low quality, resulting in a substandard data set with a too low resolution < 0.43 $Å^{-1}$; however, the structure is sufficient to show connectivity and geometry despite the high final *R* value. We will only publishing the conformation of the molecule and the crystallographic data. We will not deposit the data in the Cambridge Crystallographic Data Centre. Crystallographic data as well as structure solution and refinement details are summarized in Table S1. OLEX2[S8] was used for structure representations.

Supporting Information available**:** Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2020619 for **3a**, CCDC-2020620 for **3c**, CCDC-2020621 for **4a**, CCDC-2020622 for **4b**, CCDC-2020623 for **4c**, CCDC-2020624 for **5a**, CCDC-2020625 for **5b**, CCDC-

2020626 for **5c**, CCDC-2020627 for **5d**, CCDC-2020628 for **6b**, and CCDC-2020629 for **7d**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**3a**	**3c**	**3d**	**4a**
formula	$C_{40}H_{68}Al_2N_4$	$C_{42}H_{72}Al_2N_4$	$C_{46}H_{72}Al_2N_4$	$C_{40}H_{66}Al_2N_6$
fw ($g \cdot mol^{-1}$)	658.94	686.99	735.03	684.94
T/°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	P 2_1/n	P 2_1/n	P 2_1/c	P 2_1/n
a/ Å	9.1318(2)	9.79107(15)	18.2714(8)	9.8164(2)
b/ Å	13.1042(3)	15.9345(2)	15.6171(5)	14.8423(2)
c/ Å	17.6741(3)	13.7124(3)	16.4947(6)	14.3275(3)
α/°	90	90	90	90
β/°	103.849(2)	93.7704(16)	102.716(4)	96.659(2)
γ/°	90	90	90	90
V/$Å^3$	2053.49(8)	2134.72(6)	4591.2(3)	2073.40(7)
Z	2	2	4	2
ρ ($g \cdot cm^{-3}$)	1.066	1.069	1.063	1.097
μ (cm^{-1})	8.54	8.39	8.12	8.79
measured data	11805	22674	6009	13771
data with I > 2σ(I)	3693	3863	2319	3569
unique data (R_{int})	3998/0.0188	4231/0.0353	3014/0.029	4086/0.0299
wR_2 (all data, on	0.0936	0.0962	0.0805	0.0961
R_1 ($I > 2\sigma(I)$) [a]	0.0337	0.0349	0.0403	0.0355
S [b]	1.036	1.046	1.063	1.046
Res. dens./$e \cdot Å^{-3}$	0.278/-0.217	0.281/-0.224	0.130/-	0.291/-0.237
absorpt method	gaussian	gaussian	analytical	gaussian
absorpt corr	0.918/0.952	0.868/0.947	0.966/0.990	0.901/0.942
CCDC No.	2020619	2020620	motif	2020621
Compound	**3a**	**3c**	**3d**	**4a**

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**4b**	**4c**	**5a**	**5b**
formula	$C_{41}H_{68}Al_2N_6$	$C_{42}H_{70}Al_2N_6$	$C_{36}H_{56}Al_2I_4N4$	$C_{37}H_{58}Al_2I_4N$
fw ($g \cdot mol^{-1}$)	698.97	713.00	1106.40	1120.43
T/°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	orthorhombic	monoclinic	triclinic	triclinic
space group	P c c n	P 2_1/n	P ī	P ī'
a/ Å	29.8017(5)	10.1444(2)	9.5939(3)	10.2273(2)
b/ Å	18.1453(4)	15.2810(4)	10.3764(3)	13.8795(3)
c/ Å	15.8102(3)	14.1282(4)	12.9532(4)	17.1873(4)
α/°	90	90	75.031(3)	66.377(2)
β/°	90	91.173(2)	75.198(3)	86.7647(19)
γ/°	90	90	64.216(3)	87.4261(19)
V/Å^3	8549.5(3)	2189.65(9)	1106.42(7)	2231.06(10)
Z	8	2	1	2
ρ ($g \cdot cm^{-3}$)	1.086	1.081	1.661	1.668
μ (cm^{-1})	8.62	8.49	227.04	225.27
measured data	29700	14847	14271	25102
data with I > 2σ(I)	7109	3925	4103	7720
unique data (R_{int})	8496/0.0279	4310/0.0232	4341/0.0420	8791/0.046
wR_2 (all data, on	0.1167	0.0969	0.0805	0.0900
R_1 ($I > 2\sigma(I)$) [a]	0.0415	0.0356	0.0290	0.0341
S [b]	1.037	1.035	1.053	1.037
Res. dens./e·Å^{-3}	0.271/-0.236	0.263/-0.200	0.931/-1.062	0.692/-
absorpt method	gaussian	gaussian	gaussian	gaussian
absorpt corr	0.848/0.918	0.879/0.951	0.097/0.235	0.115/0.465
CCDC No.	2020622	2020623	2020624	2020625

cont. Table S1: Crystal data and refinement details for the X-ray structure determinations.

Compound	**5c**	**5d**	**6b**	**7d**
formula	$C_{38}H_{60}Al_2I_4N_4$	$C_{42}H_{60}Al_2I_4N_4$	$C_{37}H_{56}Al_2I_4N_6$ [*]	$C_{42}H_{60}Al_2Cl_4$
fw ($g \cdot mol^{-1}$)	1134.46	1182.50 [*]	1146.43 [*]	816.70
°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	Triclinic	orthorhombic	monoclinic
space group	P 2_1/n	P ī	P b c n	P 2_1/c
a/ Å	10.1421(2)	9.4936(3)	17.8187(3)	17.8904(2)
b/ Å	16.2451(3)	16.5995(4)	17.3288(2)	15.60507(14
c/ Å	13.8772(3)	18.3183(5)	16.6003(3)	16.45733(19
α/°	90	63.478(3)	90	90
β/°	95.334(2)	85.190(3)	90	101.7305(12
γ/°	90	89.826(3)	90	90
V/Å^3	2276.50(8)	2571.96(14)	5125.78(14)	4498.60(9)
Z	2	2	4	4
ρ ($g \cdot cm^{-3}$)	1.655	1.527 [*]	1.486 [*]	1.206
μ (cm^{-1})	220.85	24.87 [*]	145.93 [*]	30.15
measured data	13133	10326	47117	33016
data with I > 2σ(I)	4090	9320	6703	7842
unique data (R_{int})	4508/0.0339	10326/0.0224	7026/0.0533	8841/0.023
wR_2 (all data, on	0.0606	0.0854	0.0678	0.0801
R_1 ($I > 2\sigma(I)$) [a]	0.0251	0.0296	0.0256	0.0296
S [b]	1.024	1.030	1.052	1.038
Res. dens./e·Å^{-3}	0.563/-0.619	1.245/-0.632	1.128/-0.930	0.309/-
absorpt method	gaussian	multi-scan	gaussian	gaussian
absorpt corr	0.165/0.399	0.93943/1.000	0.059/0.344	0.525/0.768
CCDC No.	2020626	2020627	2020628	2020629

[*] derived parameters do not contain the contribution of the disordered solvent.

[a] Definition of the *R* indices: $R_1 = (\Sigma \| |F_o| - |F_c| \|)/\Sigma |F_o|$;
$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$;
[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

References

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[S8] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.*, **2009**, *42*, 339.

6. Synthesis of magnesium dications as super Lewis-acids

6.1 Introduction

Lewis acidity plays a pivotal role in the homogenous catalysis of alkaline-earth metals. Due to their lack of d-orbitals and their incapacity of fast and reversible oxidation state changes, the catalytic activity is strongly dependent on the nucleophilic and/or basic behavior of the catalysts´ active group (R) and the substrate activation by the metal center (AE), Figure 1.[1]

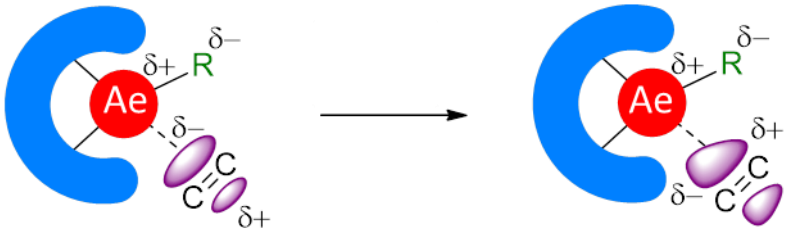


Figure 1 Exemplarily Lewis-acidic activation of a C-C double bond. Ae = alkaline-earth metal.

As a consequence, researches became interested in maximizing the Lewis acidity on the metal center by removal of the active group, to form cationic complexes. Following that idea, a variety of cationic alkaline-earth metal complexes have been reported and successfully applied in catalytic transformations such as polymerizations,[2] olefin hydrogenations[3] and hydrosilylations.[4] Most of these cations contain either boron-hydride counter ions with rather short metal-hydride contacts or coordinated oxygen- and nitrogen-based Lewis bases, which significantly decreases the Lewis acidity of the metal center. In 2018, the workgroups of Harder and Hill almost simultaneously reported groundbreaking "naked" magnesium and calcium based cations involving $B(C_6F_5)_4^-$ (Harder) and $[Al\{OC(CF_3)_3\}_4]^-$ (Hill) counterions,[1,5] Figure 2.

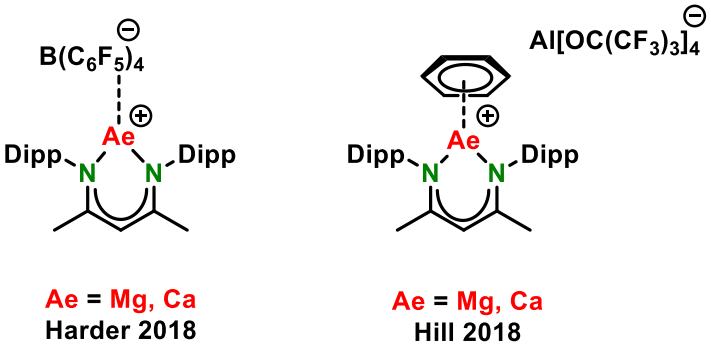


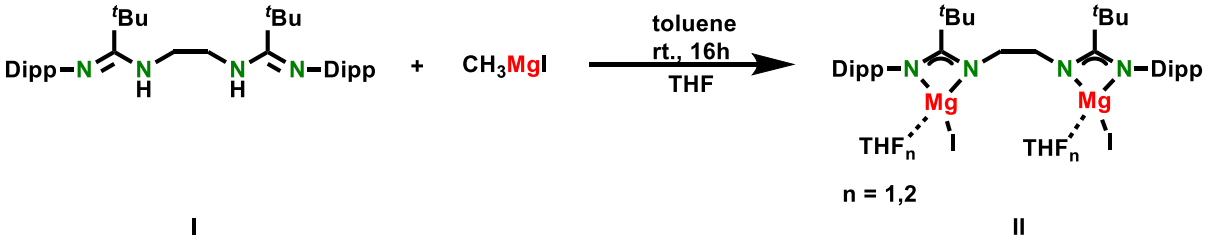
Figure 2 "Naked" magnesium and calcium cations.

Since then these complexes proved their outstanding Lewis acidity as reports about the coordination of arenes, alkenes, alkynes, phosphines and even silyl ethers, which are usually inert with respect to metal bonding, have been published.[5,6] Encouraged by the results of this novel research area, attempts to form analogous magnesium dications based on an ethylene bridged bis(amidine) ligand have been performed.

6.2 Results and discussion

Metal complex precursor synthesis

The starting complex for the synthetic approaches of the magnesium dication formation is the heteroleptic magnesium-iodide complex (**II**, see also chapter 3) based on an ethylene-bridged bis(amidine) ligand (**I**), Scheme 1.



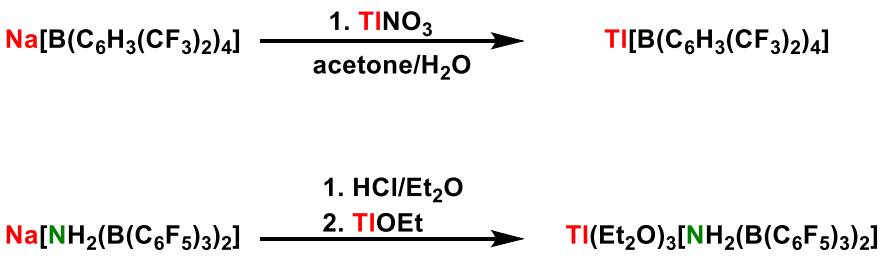
Scheme 1 Synthesis of the starting complex **II**.

Therefore, the respective protio-ligand (**I**) was treated with a solution of CH_3MgI (3.0 M in Et_2O) in toluene and stirred at room temperature for 16 hours. Afterwards the solution was concentrated and a few drops of THF were added to obtain complex **II** as colorless crystals with four coordinated THF molecules. Upon drying under vacuum two THF molecules can be further removed to obtain two tetra coordinated magnesium centers.

As already debated, complex **II** is insoluble in hydrocarbon solvents as well as diethyl ether and undergoes Schlenk-type rearrangement reactions once dissolved in THF. Therefore, and on the basis of the results of Harder and coworkers all further investigations on the dication formation were performed in chloro- or bromobenzene.

Thallium salt precursor synthesis

To follow a procedure of Harder and coworkers[6b] a variety of thallium salts of weakly coordinating anions for salt metathesis reactions were synthesized. Therefore literature known procedures have been adopted to isolate $Tl[B(C_6H_3(CF_3)_2)_4]$ ($TlBArF_{24}$)[7] and $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$[8], Scheme 2.

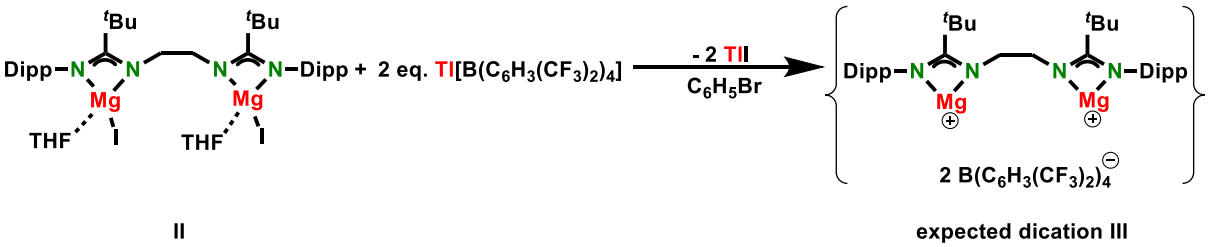


Scheme 2 Literature known synthesis of thallium salts of weakly coordinating anions.

Starting from $Na[NH_2(B(C_6F_5)_3)_2]$ treatment with HCl gas in Et_2O led to the formation of $[H(Et_2O)_2[NH_2(B(C_6F_5)_3)_2]]$ which was further converted *in situ* with TlOEt to obtain $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ as a white solid. The starting material $Na[NH_2(B(C_6F_5)_3)_2]$ was prepared by the reaction of $NaNH_2$ and $B(C_6F_5)_3$ prior to use. $TlBArF_{24}$ was prepared by an simple salt metathesis reaction using thallium(I)nitrate and $Na[B(C_6H_3(CF_3)_2)_4]$ and isolated as a white solid.

Magnesium dication isolation attempts

The first attempts for the isolation of the magnesium dication from complex **II** was the treatment of **II** with $TlBArF_{24}$. Therefore two equivalents of the thallium salt were added to a solution of **II** in bromobenzene and stirred for 30 minutes at room temperature, Scheme 3. Upon addition of the pure white salt to the colorless solution an instant color-change from white to yellow of the solid was observed. This observation indicates the formation of the desired thallium iodide (yellow) and thus the successful ligand exchange of the counter ions. After filtration, the remaining solution was concentrated to obtain a yellow oily product. Interestingly, dissolving the oil in C_6D_6 leads to the formation of a biphasic system indicating strong electron repulsions within the product. However, NMR measurements conducted in C_6D_5Br gave a slightly yellow, homogeneous solution.



Scheme 3 Attempted synthetic pathway for the isolation of the expected but not evidenced dication **III**.

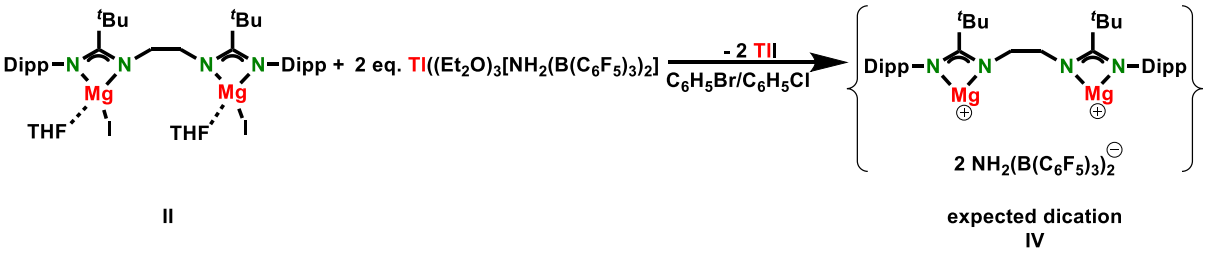
The analysis of the obtained NMR spectra may give evidence to the formation of the desired dicationic complex. The ^{19}F NMR spectra (C_6D_6 and C_6D_6/C_6D_5Br) as well as the ^{11}B NMR

spectra (C_6D_6 and C_6D_6/C_6D_5Br) show strong singlet peaks at -62.6 ppm and -6.1 ppm, respectively, which can be assigned to the $[B(C_6H_3(CF_3)_2)_4]^-$ anion, Figure S1-S3. Considering the insolubility of $TlBArF_{24}$ in C_6D_6 as well as C_6D_5Br and the general reaction procedure (removal of all remaining solids by filtration) the formation of a soluble, $BArF_{24}^-$ anion containing species is in all likelihood.

Encouraged by the results of the NMR analysis several procedures to obtain crystals suitable for X-Ray diffraction measurements have been performed. The oily product was layered with hexanes and left for crystallization either at room temperature or -23 °C for several months. In a different approach the oil was diluted in a small amount of C_6H_5Br followed by layering with hexanes and standing at room temperature for several months. Also the slow evaporation of hexane into NMR tubes containing a concentrated solution of the product in C_6D_6 as well as C_6D_6/C_6D_5Br has been tested. Unfortunately, all crystallization experiments remained unsuccessful even after repeated attempts. Even though analytical data strongly suggests the formation of a dicationic species, final structural proof of its existence by X-ray diffraction analysis is yet to be done.

As the results of the $TlBArF_{24}$ reactions turned out to be very promising slight changes concerning the counter anion were conducted in order to improve the crystallization ability. Therefore, the $TlBArF_{24}$ salt was replaced by the $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ salt as the respective counter anion $NH_2(B(C_6F_5)_3)_2^-$ is assumed to exhibit better crystallization properties. Another important advantage is the solubility of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ in C_6H_5Br and C_6H_5Cl, which makes it easier to follow the reaction progress.

A solution of the starting material complex **II** in C_6H_5Cl or C_6H_5Br was treated with a solution of two equivalents of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ in C_6H_5Cl and C_6H_5Br, respectively, leading to the instantaneous formation of a yellow precipitate, similar to the reactions involving $TlBArF_{24}$, Scheme 4. Filtration and solvent removal again gave an oily yellow product.



Scheme 4 Attempted synthetic pathway for the isolation of the expected but not evidenced dication **IV**.

Similar to the previous observations, dissolving the oily product in C_6D_6 results in a biphasic system, whereas C_6D_5Br as a solvent supported the formation of a homogenous solution. Interestingly, the NMR spectra measured in C_6D_6 show a well-defined proton spectrum assignable to the protonated ligand, whereas only low ^{19}F and no ^{11}B signal could be observed, Figure S4-S6. Addition of C_6D_5Br and thus formation of a homogenous solution lead to a more diffuse proton NMR spectrum and a well-defined ^{19}F NMR spectrum showing the expected three signals for $NH_2(B(C_6F_5)_3)_2^-$, Figure S7. To gain deeper insight in the product mixture, the yellow oil was extracted with Et_2O, dried under vacuum and the resulting oil was analyzed *via* NMR spectroscopy. The proton NMR spectrum shows well-defined, but not assignable signals, Figure S8. Mentionable, the ^{19}F spectrum as well as the ^{11}B spectrum show three (-132.3, -158.9 and -164.5 ppm) and one (-16.2 ppm) strong peaks, respectively, which are expected for the $NH_2(B(C_6F_5)_3)_2^-$ anion, Figure S9-S10.

Encouraged by the observations and the well-defined NMR spectra, various attempts for the isolation of crystals suitable for X-Ray diffraction measurements have been conducted. Similar to the previous experiments, the crude oily product and the diethyl ether extracted product were layered with pentane followed by standing at room temperature for several months. Another attempt was performed similar to the descriptions of the Harder group [6b], where a spatula was used to carefully scratch the glass-wall of the oily product containing flask to initiate crystallization. Unfortunately, none of these methods led to the formation of crystals so far. Once again there is strong evidence for the formation of the desired complex **IV**, but its certain existence and structural conformation could not be determined yet.

6.3 Conclusion

The heteroleptic dinuclear complex **II** was treated with the thallium salts of the weakly coordinating anions $TlBArF_{24}$ and $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ aiming for a salt metathesis reaction to get access to the respective magnesium dications. Observations during the reactions as well as the ^{1}H, ^{19}F and ^{11}B NMR spectra give reasonable evidence for the formation of the desired products. Nevertheless, the structural conformation of the reaction products could not be determined by further characterization methods as no crystals suitable for X-Ray diffraction measurements could be isolated so far. Future investigations on this reaction may be performed *in situ* without previous isolation of complex **II** in order to prevent the coordination of two Lewis-basic THF molecules to the metal centers. These strongly coordinating solvents could possibly disturb the reaction and thus the formation of the desired products **III** and **IV**.

6.4 References

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6.5 Supporting information

General

All inorganic preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line or glovebox techniques (Mb 200G). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally through P_4O_{10}. Toluene, diethyl ether, *n*-pentane and *n*-hexane were freshly collected from a solvent purification system by M. Braun (MB SPS- 800). D_6-Benzene and C_6D_5Br were used as p.a. grade and were distilled from Na/benzophenone prior to use.

Dry C_6H_5Cl was purchased from Sigma- Aldrich, whereas TlBarf24,[S1] $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$[S2] and complex **II**[S3] were prepared according to literature known procedures.

Characterization. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C), BF_3 Et_2O (^{11}B) and CFCl3 (^{19}F). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak (C_6D_6: δ(^1H) = 7.16) and the solvent peak (C_6D_6: δ(^{13}C) = 128.06).

General reaction procedure for the reaction of II with $TlBarf_{24}$:

Solid $TlBarf_{24}$ (500 mg, 0.44 mmol, 1 eq.) was added to a stirred solution of **II** (943 mg, 0.88 mmol, 2 eq.) in C_6H_5Br (10 mL) causing an instant color change of the solid from white to yellow. After stirring for 30 minutes, the solid was filtered off and the solvent was removed in vacuum to obtain the raw product as a yellow oil.

General reaction procedure for the reaction of II with $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$:

A solution of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ (593 mg, 0.41 mmol, 2 eq.) in C_6H_5Br or C_6H_5Cl (2 mL), respectively, was added to a stirred solution of **II** (200 mg, 0.20 mmol, 1 eq.) in C_6H_5Br or C_6H_5Cl (2 mL), respectively, causing an instant formation of a yellow precipitate. After stirring for 30 minutes, the solid was filtered off and the solvent of the remaining solution was removed to obtain the raw product as a yellow oil, which was further extracted with Et_2O to obtain an oily product.

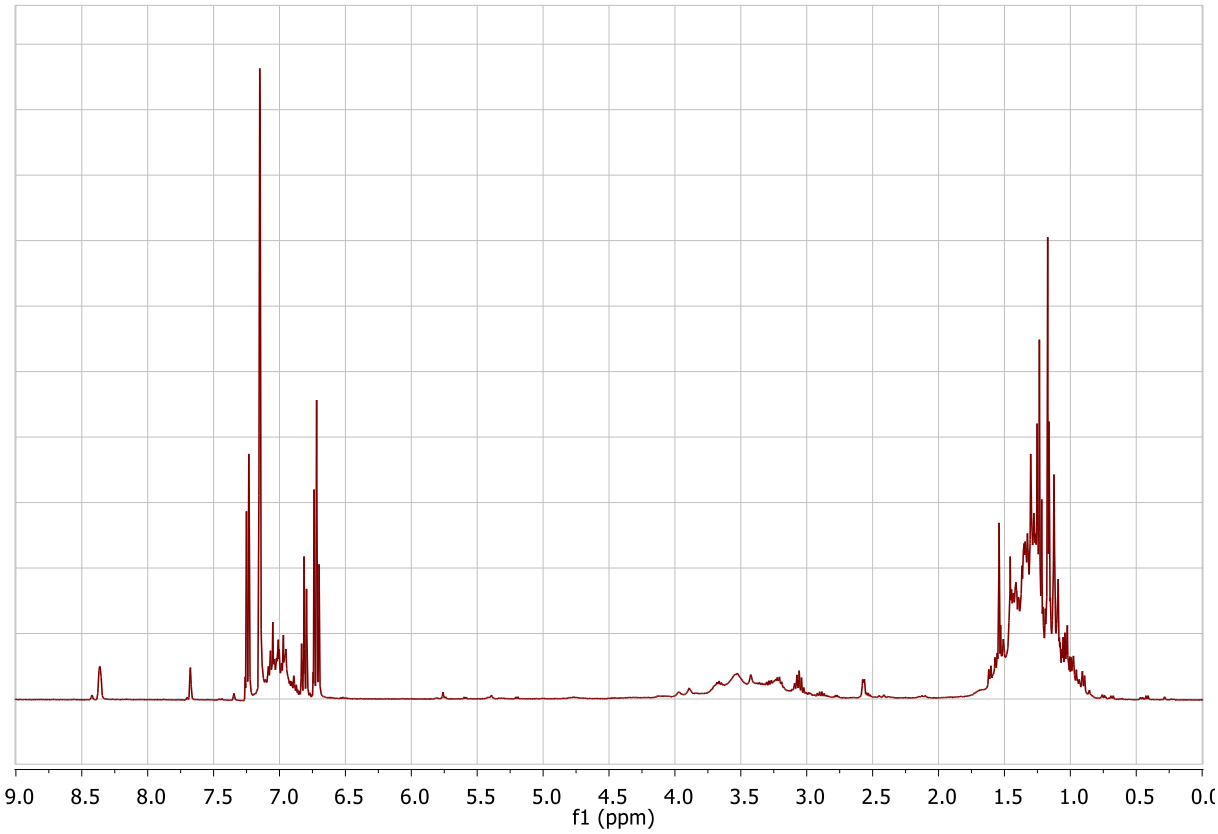

Figure S1 ^{1}H NMR spectrum (400 MHz) of the reaction of $TlBarf_{24}$ with **II** in C_6D_6/C_6D_5Br.

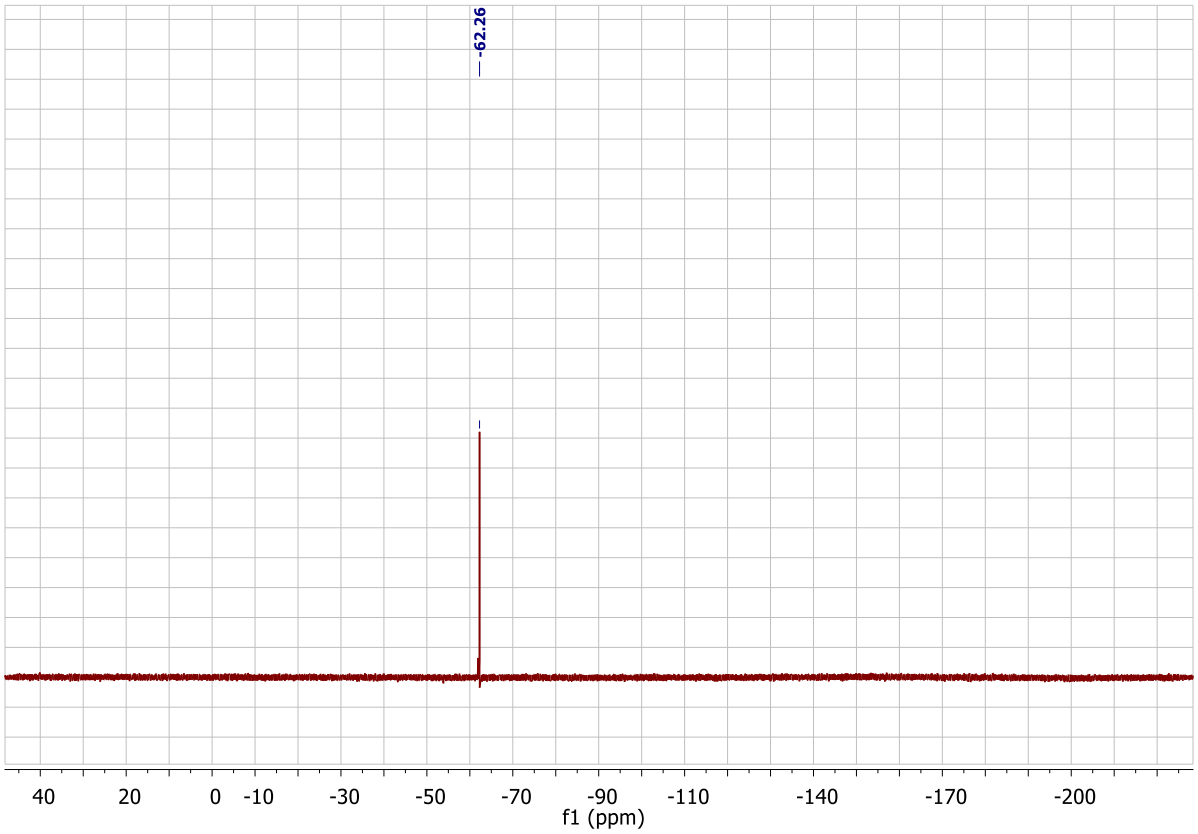

Figure S2 ^{19}F NMR spectrum (377 MHz) of the reaction of $TlBarf_{24}$ with **II** in C_6D_6/C_6D_5Br.

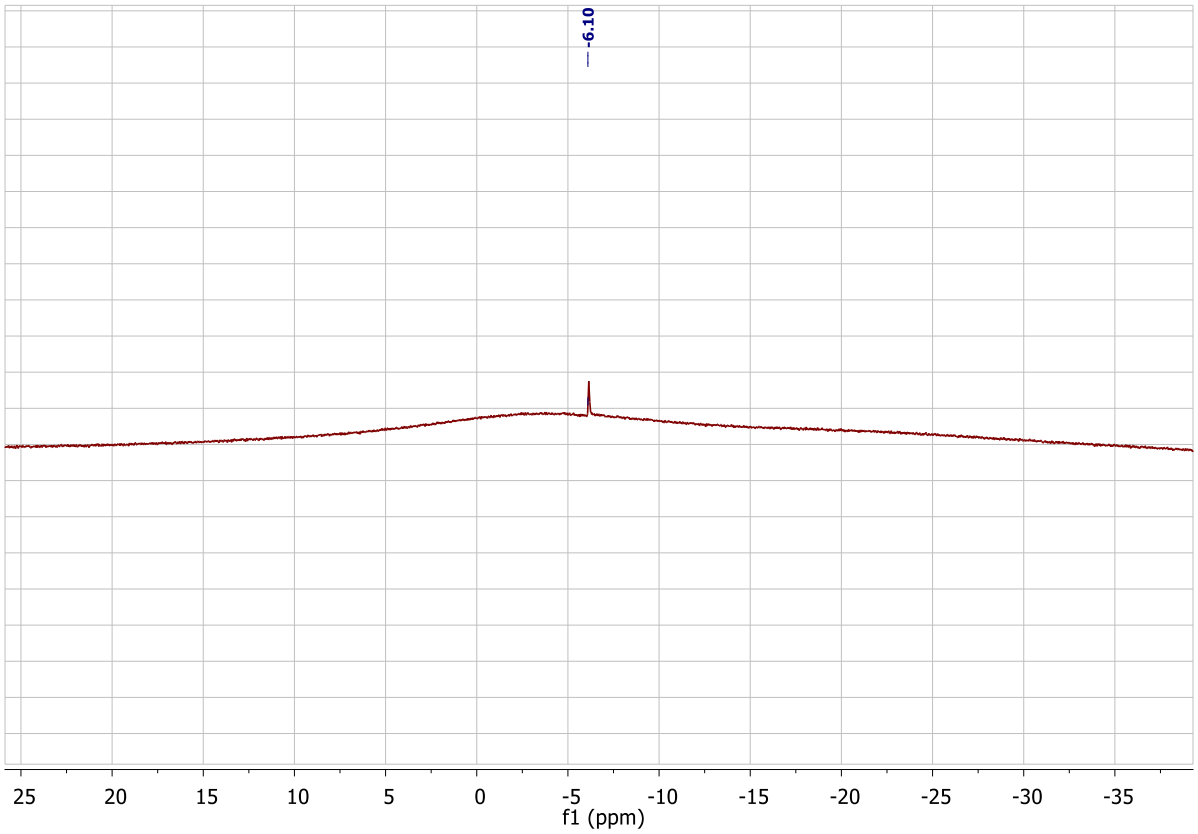

Figure S3 ^{11}B NMR spectrum (128 MHz) of the reaction of $TlBarf_{24}$ with **II** in C_6D_6/C_6D_5Br.

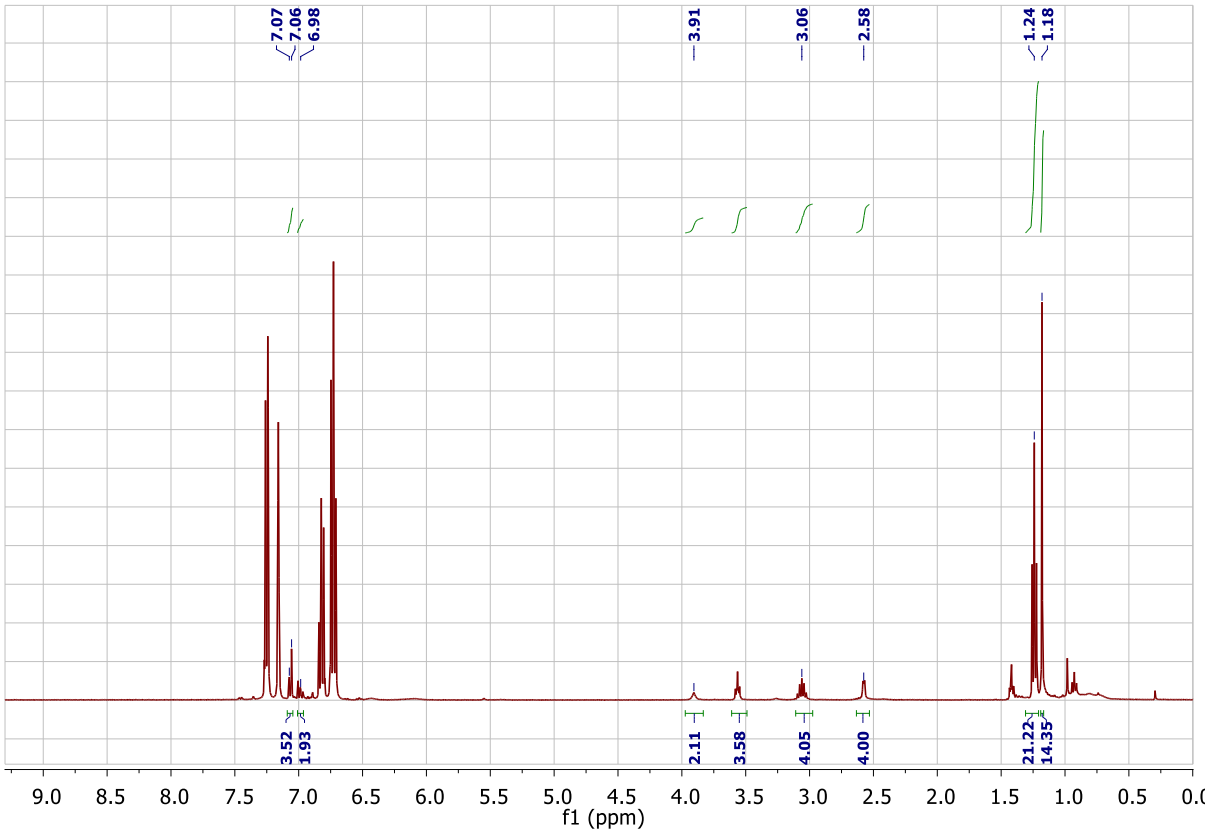

Figure S4 ^{1}H NMR spectrum (400 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6.

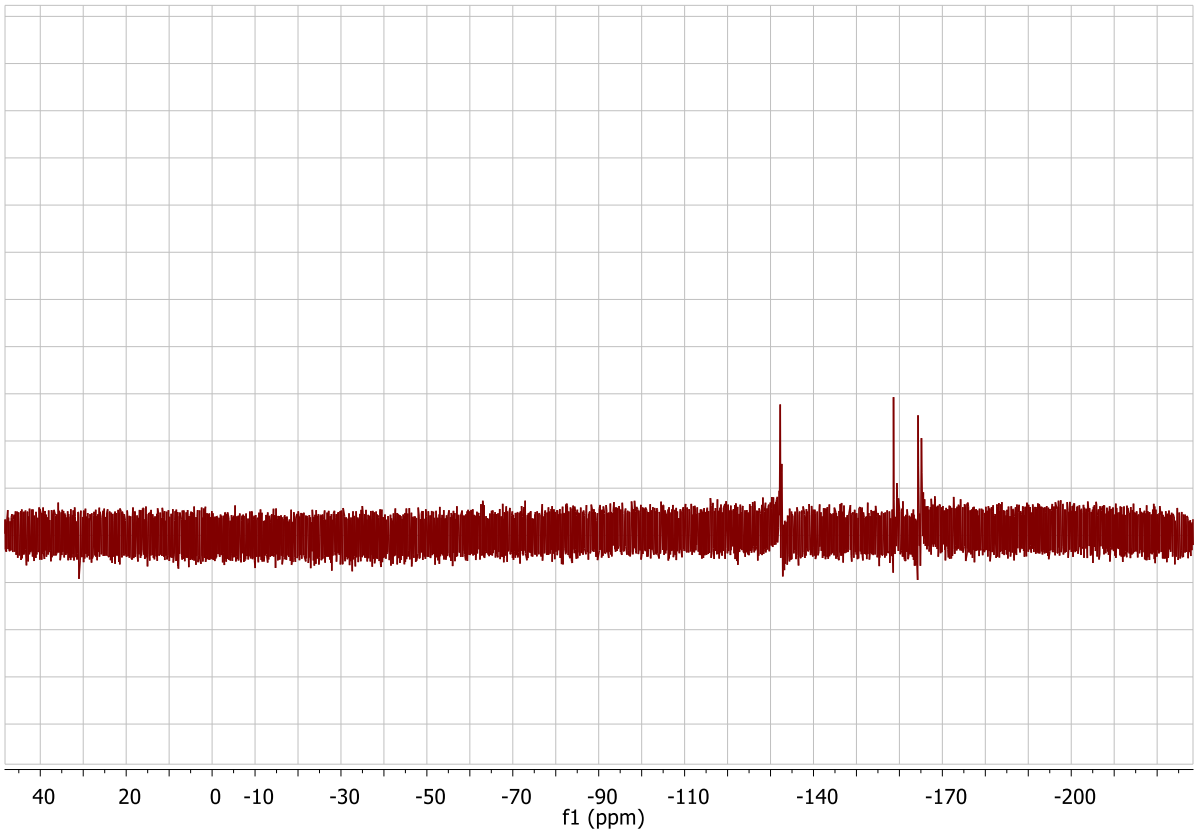

Figure S5 ^{19}F NMR spectrum (377 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6.

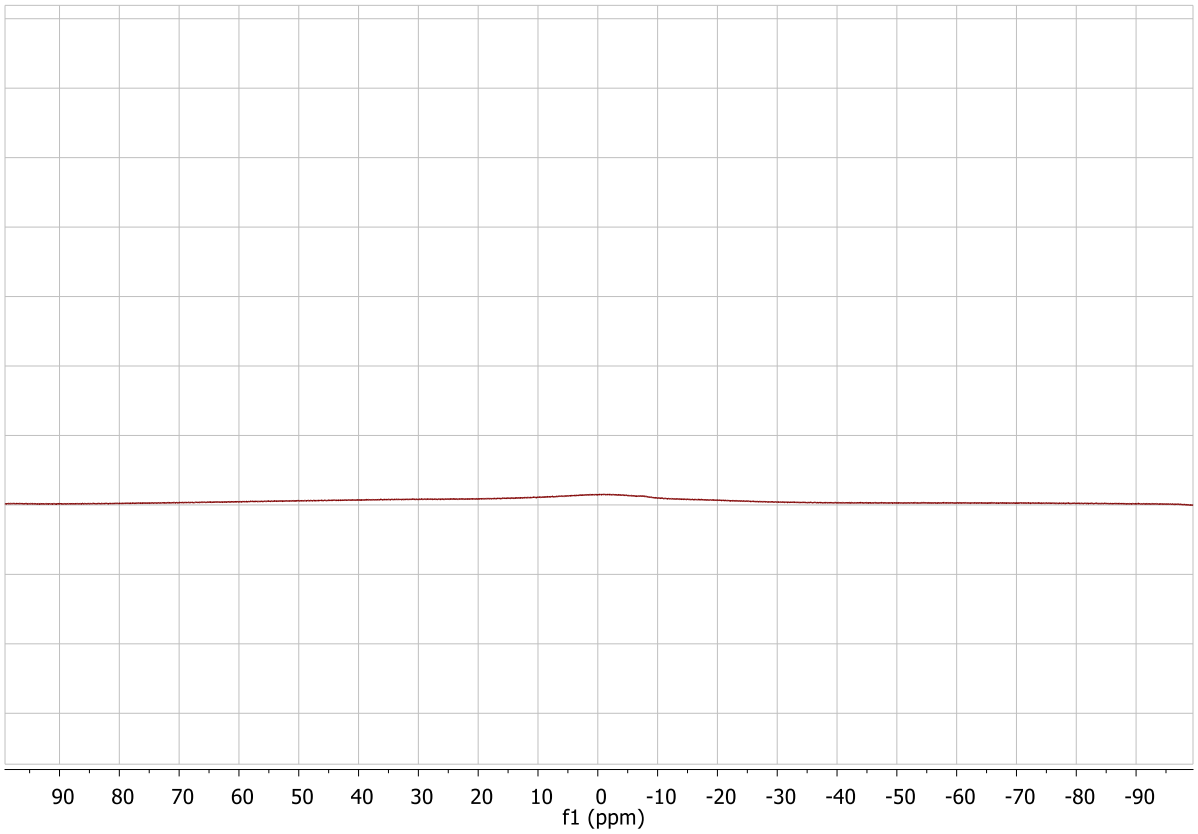

Figure S6 ^{11}B NMR spectrum (128 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6.

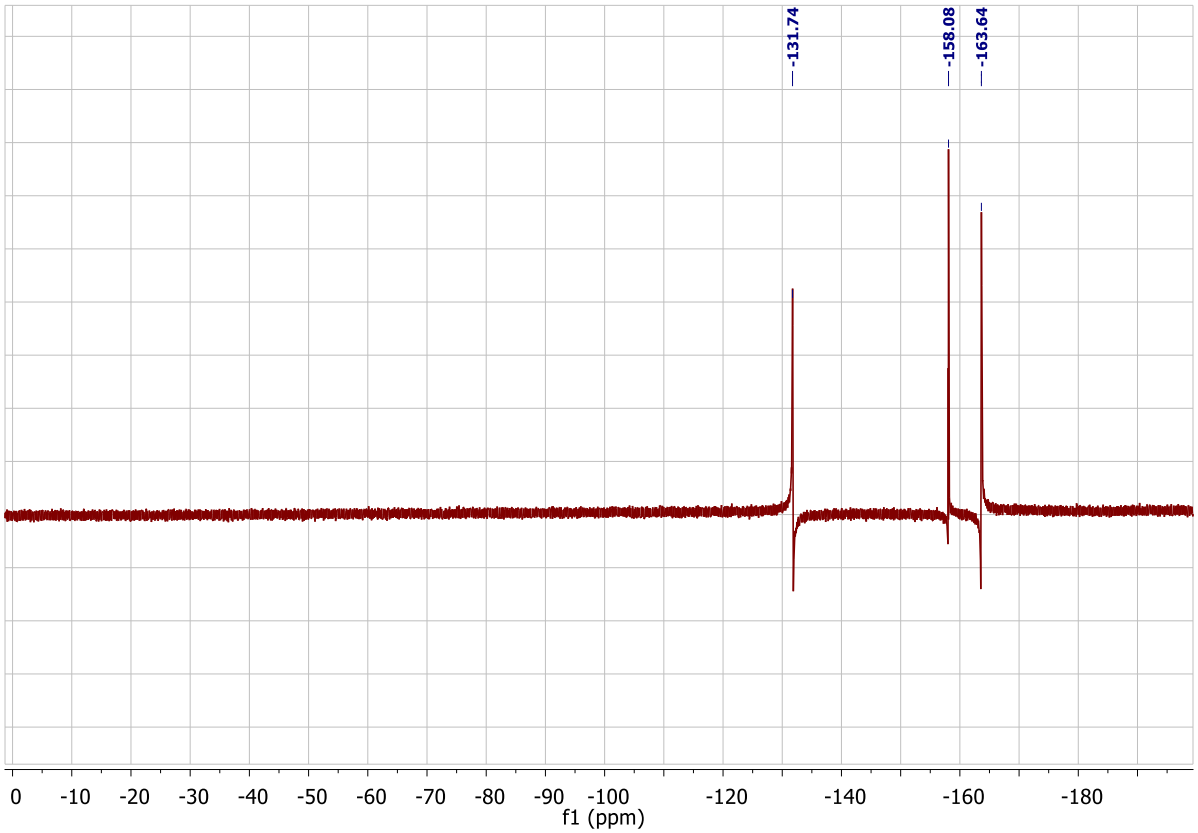

Figure S7 ^{19}F NMR spectrum (377 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6/C_6D_5Br.

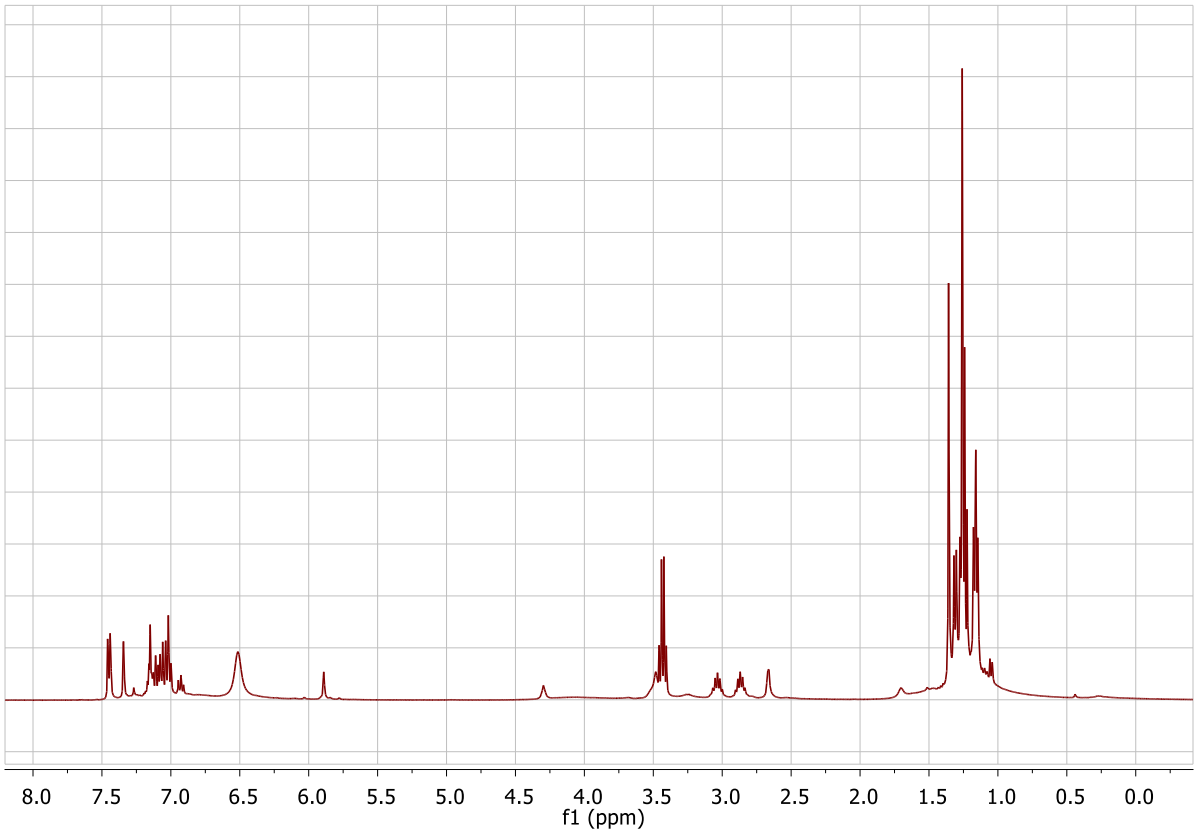

Figure S8 ^{1}H NMR spectrum (400 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6/C_6D_5Br after Et_2O extraction.

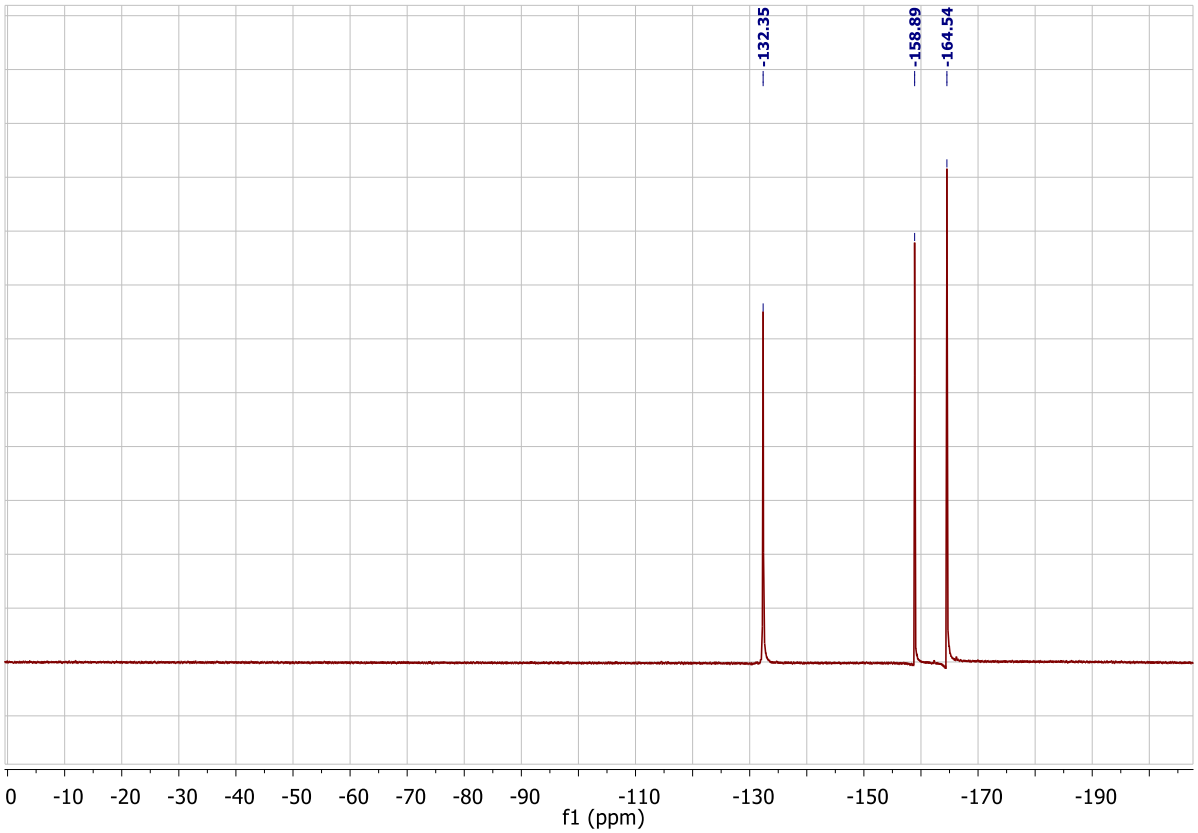

Figure S9 ^{19}F NMR spectrum (377 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6/C_6D_5Br after Et_2O extraction.

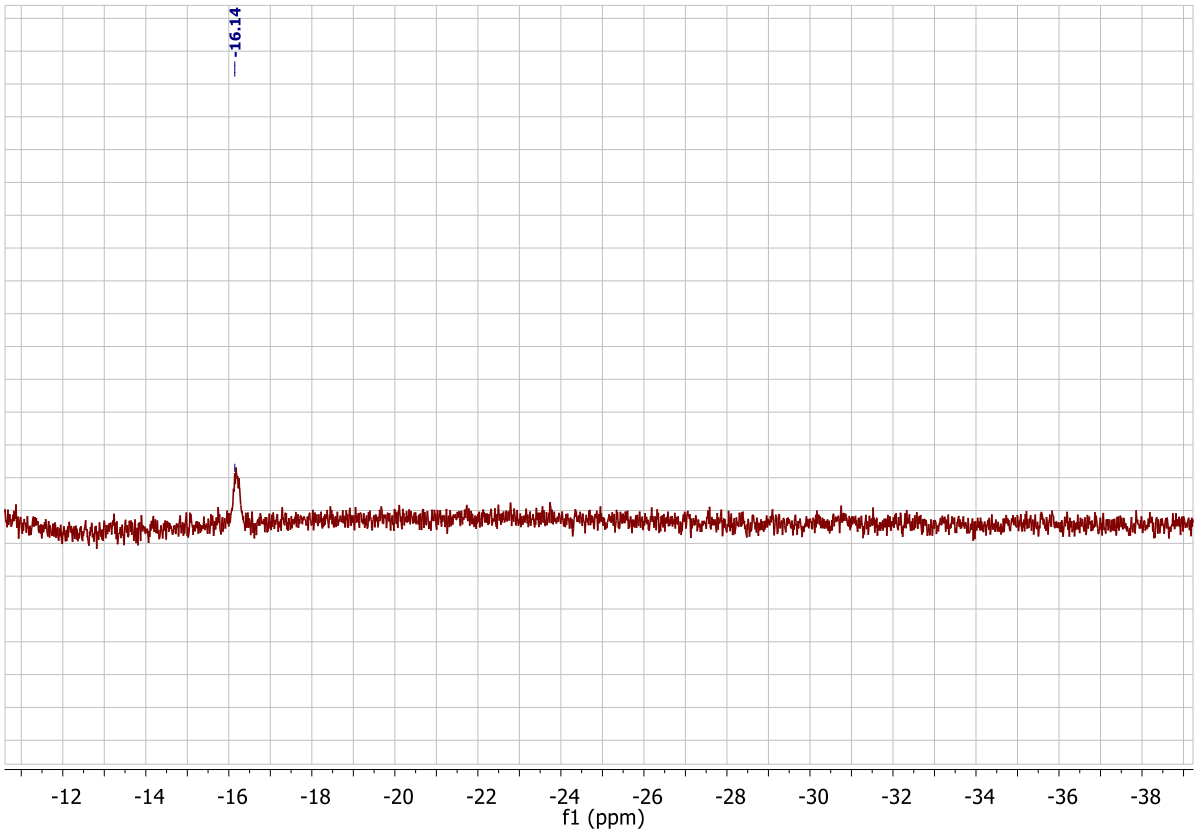

Figure S10 ^{11}B NMR spectrum (128 MHz) of the reaction of $Tl((Et_2O)_3[NH_2(B(C_6F_5)_3)_2]$ with **II** in C_6D_6/C_6D_5Br after Et_2O extraction.

References

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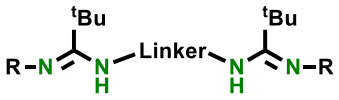
7. Conclusion

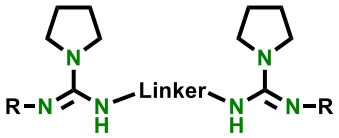
This work gives an insight in the uprising research area of dinuclear main-group metal complexes. Besides the description of innovative and highly efficient reaction pathways to access dinucleating bis(amidine)s, bis(guanidine)s and bis(amidoamine)s in good to excellent yields, also 37 mono- and dinuclear complexes of the respective ligands have been isolated and characterized. Additionally, first catalytic experiments, namely the ring-opening polymerization of ε-caprolactone and L-lactide, foreshadow the high potential of these novel dinuclear complexes in catalytic transformations.

Protio-ligand synthesis

The proper design of ligand frameworks is the key towards the isolation of dinuclear metal complexes. Not only the coordination abilities or the sterically properties, but especially the metal-metal distance within the complex play a crucial role for the appearance of cooperative effects and thus the improved catalytic potential compared to their mononuclear relatives. Therefore, a variety of novel and easy tunable *N*,*N*-chelating ligands, which can be synthesized in big-scale reactions, has been introduced during this work.
The nitrogen-bridged bis(amidine)s **Ia-e** were synthesized via an aminolysis of the respective bis(imidoylchloride)s and obtained in yields between 45 to 87%, Figure 1. In addition to the bis(amidine)s also a similar set of bis(guanidine)s **IIb-f** was obtained in good yields (59 to 99%), whereas **IIa** could only be isolated as a side product in yields of 18%, Figure 1. Bearing four different alkyl and aryl linkers and four different bulky and super bulky terminal groups these sets of ligands offer optimum requirements for investigations of the linker and end group impact on the complexation and coordination behavior.



I



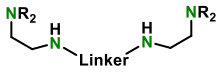
II

Linker =	ethylene	propylene	butylene	xylylene
R = Dipp	**a** (72%)	**b** (87%)	**c** (45%)	**e** (47%)
R = Dipp*		**d** (62%)		

Linker =	ethylene	propylene	butylene	xylylene
R = Dipp	**a** (18%)	**b** (98%)	**c** (81%)	**d** (99%)
R = Dmp		**e** (95%)		
R = Ph			**f** (59%)	

Figure 1 Synthesis of the ligands **Ia-d** and **IIa-f** reported during this work.

In addition to the synthesis of novel bis(amidine) and bis(guanidine) ligands, also new and innovative pathways to access the barely investigated ligand class of bis(amidoamine)s **III** and **IV** are presented during this work. The only yet reported dibenzofuran-bridged type **III** bis(amidoamine)s have been synthesized by the copper-catalyzed coupling of 4,6-diiodibenzofurane and alkylated ethylene-diamines.[C1] As this approach is limited to aromatic linker groups, alternative synthetic protocols towards the bis(amidoamine)s **III**, Figure 2, and **IV**, Figure 3, respectively, are established herein. Exhibiting a saturated backbone and, in case of **IV**, two stereogenic centers, these ligand classes have an enormous potential to serve as skeletal structures for a manifold of active catalysts.



III

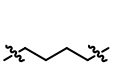
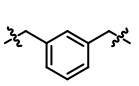
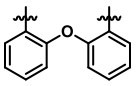
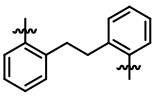
Linker =								
R = CH_3	**a** (56%)							
R = C_2H_5	**b** (41%)	**e** (45%)	**f** (88%)	**h** (76%)	**j** (72%)	**l** (63%)	**m** (51%)	**n** (63%)
R = $CH(CH_3)_2$	**c** (87%)		**g** (73%)					
R = $CH_2CH(CH_3)_2$	**d** (74%)							**o** (57%)
R = $(CH_2)_5$				**i** (73%)	**k** (56%)			

Figure 2 Overview of the different bis(amidoamine)s **III** reported in this work.

IV

Linker =	ethylene	butylene	xylylene
R = DMP, R´= $(CH_2)_2$	**a** (57%)		
R = DMP, R´= CH_3	**b** (21%)	**d** (87%)	**f** (95%)
R = Dipp, R´= CH_3	**c** (46%)	**e** (33%)	**g** (99%)

Figure 3 Overview of the different bis(amidoamine)s **IV** reported in this work.

All in all four sets of highly tunable dinucleating ligands have been introduced during this work expanding the future options for the synthesis of dinuclear element complexes.

Complex synthesis

During this work the bulk of the earlier described ligands has been applied in the synthesis of mono- and dinuclear complexes. Whereas the investigations concerning the bis(amidine)s and bis(guanidine)s were restricted to miscellaneous magnesium and aluminium based complexes, various bis(amidoamine)s of both types were treated with Mg, Zn, Al and Sn sources to get a deeper insight in the coordination behavior of this underdeveloped class of ligands.

Treatment of the bis(amidine)s **Ia-d** with different magnesium precursors ($Mg(HMDS)_2$, Mg^nBu_2, CH_3MgI) lead to the formation of the heteroleptic complex **Va** and the intermolecular homoleptic complex **VIb**, Figure 4. Mentionable, complex **Va** undergoes a Schlenk-type rearrangement upon dissolving in THF to form the homoleptic complex **VIb** and MgI_2. Similar experiments have been performed involving the bis(guanidine)s **IIa-f** leading to the isolation of complex **VIIa**, **VIId**, **VIIe** and **VIIf** as intramolecular homoleptic complexes and **VIIIb** as intermolecular homoleptic complex. As no crystals suitable for X-Ray diffraction measurements for complex **IX** could be obtained its behavior in solution was determined with means of NMR experiments. A strong solvent dependency gave varying results for solutions in toluene-d_8 and THF-d_8 and the determined diffusion coefficients gave evidence to the existence of multiple coordination compounds (type **VII**, **VIII** and **IX**) in solution, Figure 4.

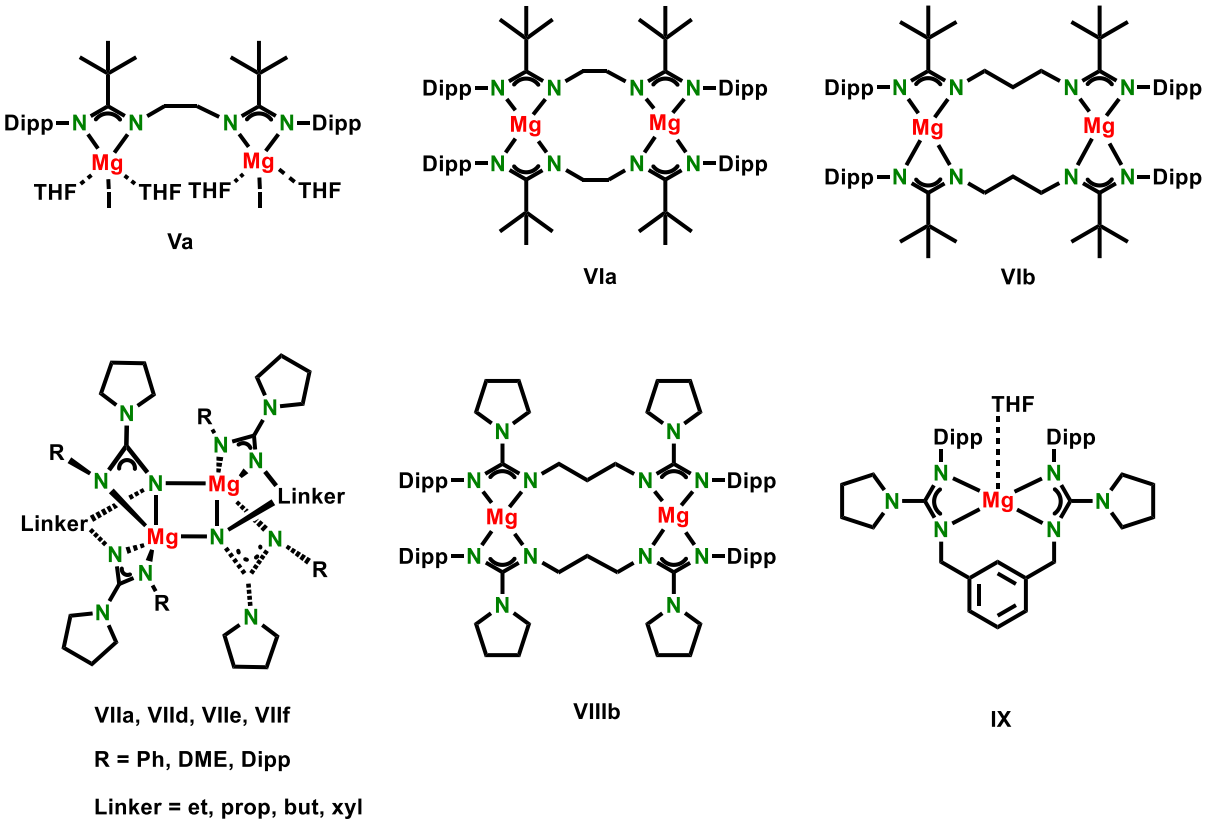


Figure 4 Bis(amidinate)- and bis(guanidinate) magnesium complexes isolated during this work.

Whereas the Schlenk-equilibrium has a strong influence on the coordination chemistry of group 2 metal complexes, treatment of the ligands **Ia-c**, **Ie** and **IIa-d** with a solution of trimethyl aluminium in toluene gives exclusively access to the respective heteroleptic complexes **Xa-c**, **Xe** and **XIa-d** in yields between 75 to 94%, Figure 5. To gain possible precursors for the synthesis of low-valent Al(I) species all aluminium alkyl complexes were further converted with elemental iodide to obtain the aluminium halide complexes **XIIa-c**, **XIIe** and **XIIIb**, Figure 5. Whereas the conversion of the bis(amidinate) complexes with yields ranging from 36 to 70% was rather smooth, the iodination of the bis(guanidinate) complexes gave complex reaction mixtures and only in the case of **XIIIb** an isolation of the desired product in 8% yield was accomplished. Additionally to the two-step reaction pathway, dinuclear aluminium halide complexes are also accessible via direct deprotonation of the protio-ligand. The reaction of **Ie** with $Al(C_2H_5)Cl_2$ lead to the isolation of the dinuclear complex **XIV** in 98% yield, Figure 5. To evaluate the aluminium halide complexes as suitable precursors for low-valent dinuclear aluminium complexes cyclic voltammetry experiments of

all five complexes have been performed. As the reduction potentials (referenced to the Fc/Fc^+ redox couple) between -3.20 and -3.25 V proved to be very low it was not surprising, that reduction attempts of the complexes **XIIc**, **XIIe** and **XIV** using either magnesium powder, cobaltocene or potassium mirror remained unsuccessful.

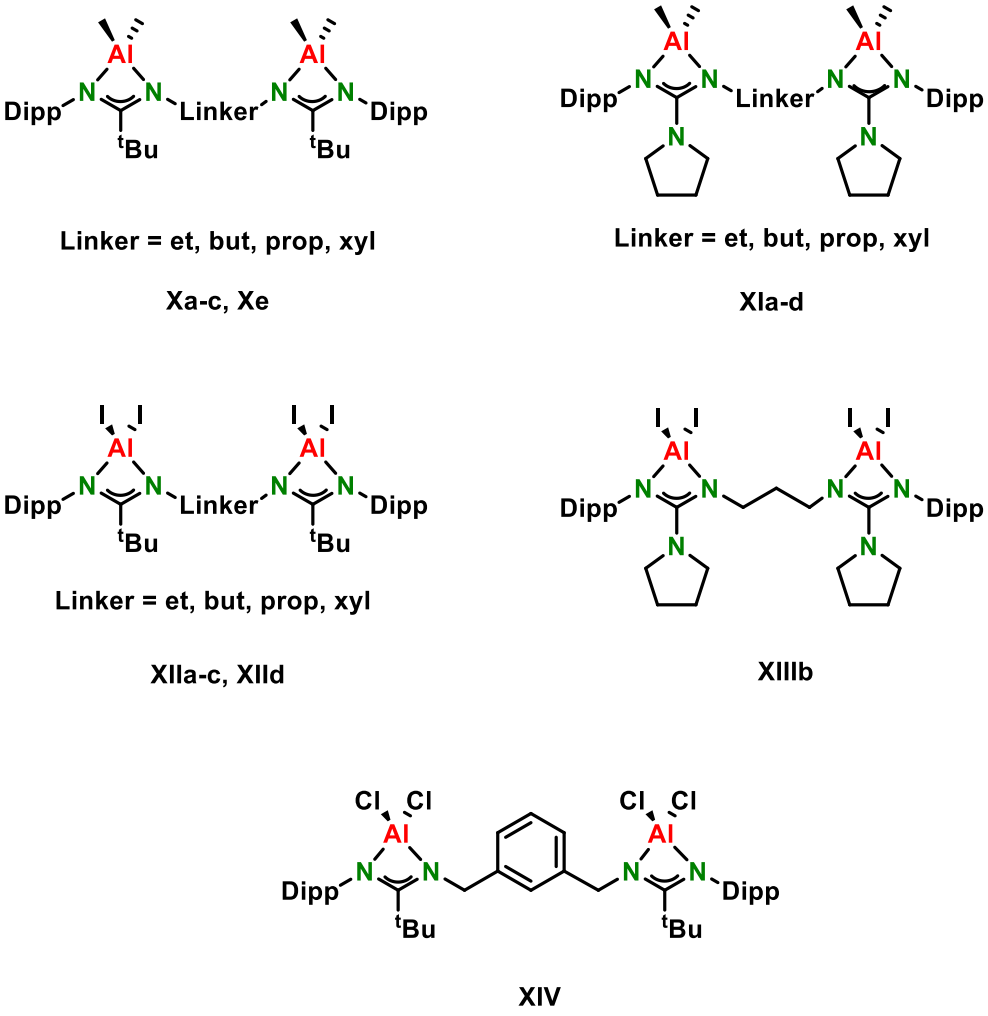


Figure 5 Dinuclear aluminium alkyl and halide complexes reported in this work.

The successful application of the complexes **X** and **XI** as catalysts in the ring-opening polymerization of ε-caprolacton and *L*-lactide gives the first evidence to the high activity of these isolated dinuclear complexes. Encouraged by these results, future investigations involving these complexes as catalysts for various reactions need to be performed.

In comparison to the bis(amidine) and bis(guanidine) ligands, which were exclusively treated with magnesium and aluminium precursors, the scope of metals was extended by tin and zinc precursors for the reaction with selected bis(amidoamine)s of the type **III** and **IV**. Consequently, conversion of **IIIj**, **IIIk**, **IIIm** and **IIIn** with $Mg(HMDS)_2$, AlH_3 NMe_3, $ZnEt_2$ and $Sn(HMDS)_2$ gave access to the respective complexes **XVn Mg**, **XVj AlH_2**, **XVk AlH_2**, **XVn Zn**, **XVm SnHMDS** and **XVn SnHMDS**, Figure 6.

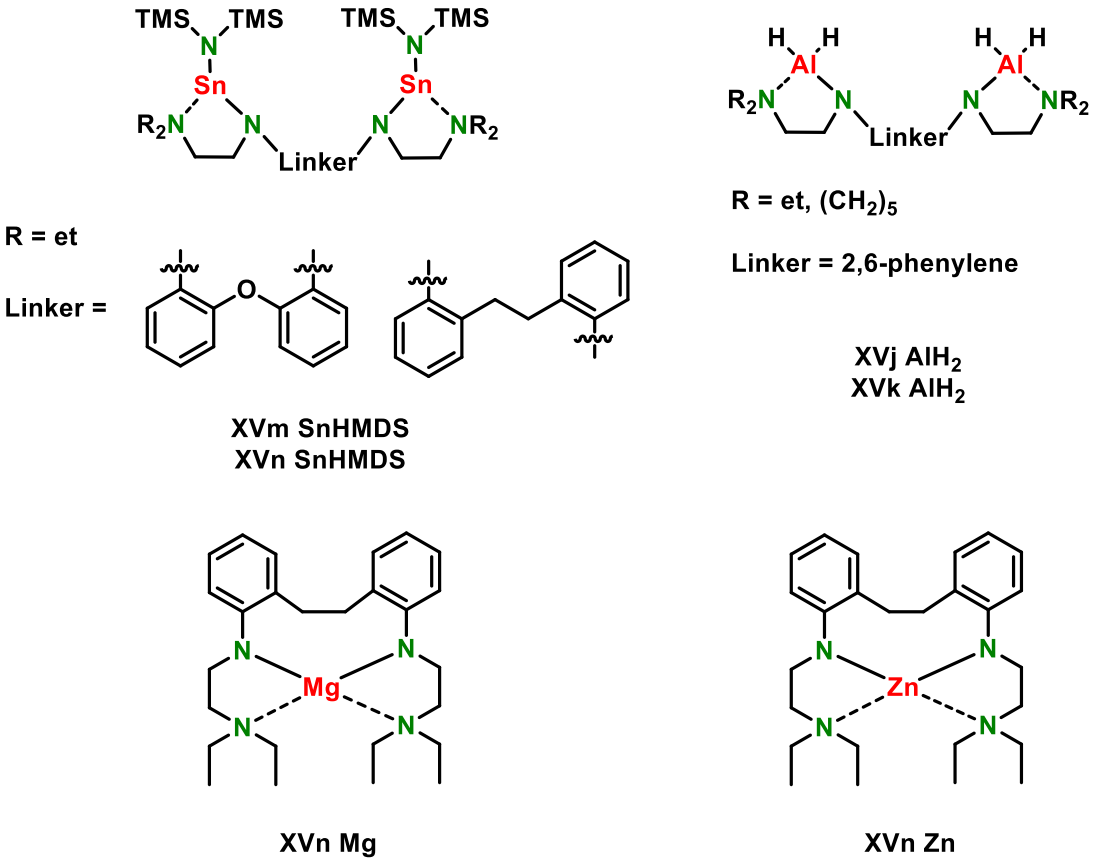


Figure 6 Mono- and dinuclear complexes of bis(amidoamine)s type **III** reported herein.

Similar to the magnesium complexes **V** to **IX**, Schlenk-type rearrangement reaction cause the formation of the mononuclear homoleptic complexes **XVn Mg** and **XVn Zn**, whereas their tin and aluminium relatives favor the formation of heteroleptic dinuclear complexes bearing two reactive sides.

Slightly deviant results were obtained during the reactions of **IVa**, **IVb** and **IVd** with $Mg(HMDS)_2$, AlH_3 NMe_3, $Al(CH_3)_3$ and $ZnEt_2$, Figure 7. Due to its rigid linker ligand **IVa** inhibits

efficiently the formation of homoleptic complexes giving access to the dinuclear heteroleptic complexes **XVIa ZnEt** and **XVIa AlMe$_2$**. In contrast ligand **IVb** heavily promotes the stabilization of homoleptic complexes. This observation is supported by the fact that treatment with both one equivalent and two equivalents of AlH_3 NMe_3 merely lead to the isolation of complex **XVIb AlH**. However, conversion of **IVb** and **IVd** with $Al(CH_3)_3$ gave the heteroleptic dinuclear complexes **XVIb AlMe$_2$** and **XVId AlMe$_2$**.

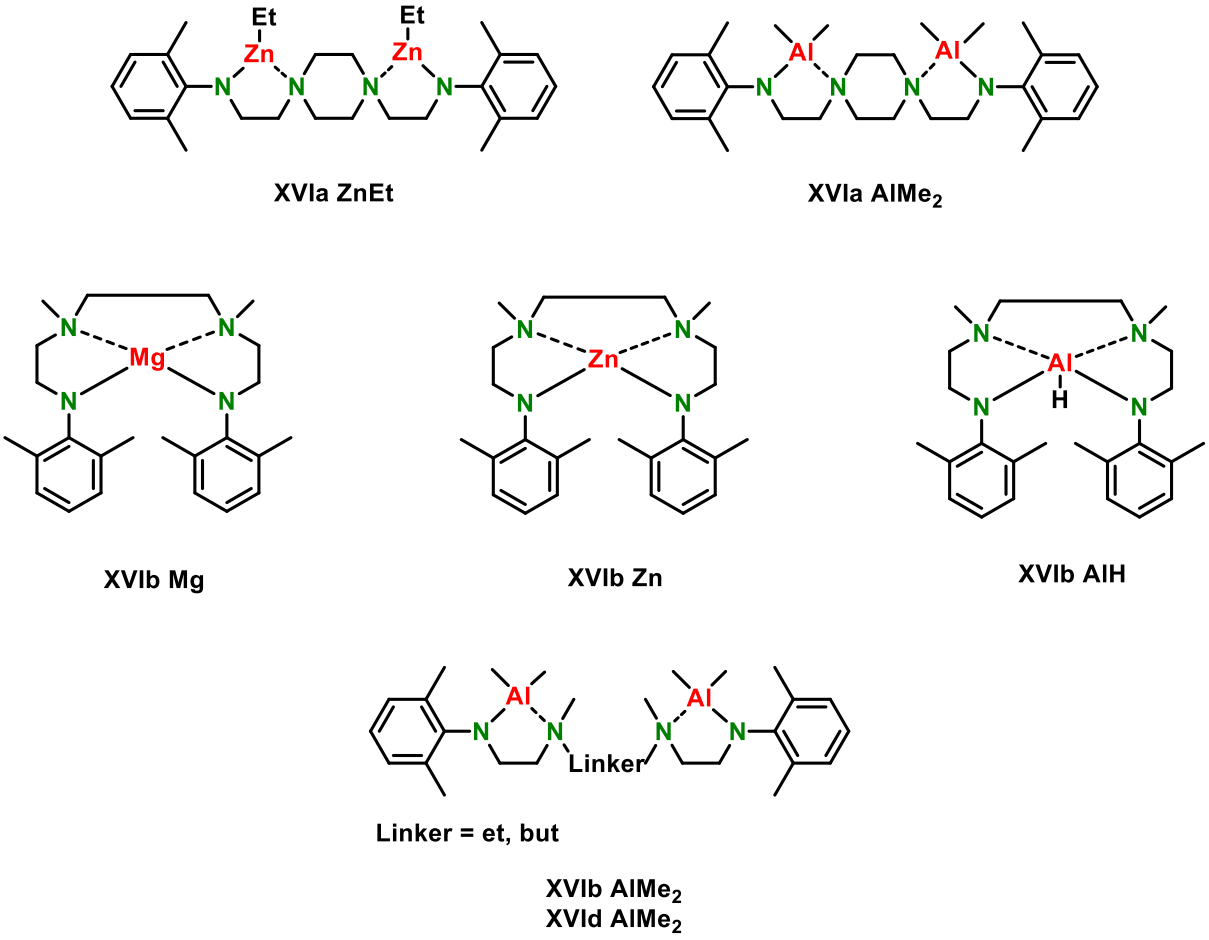


Figure 7 Mono- and dinuclear complexes of bis(amidoamine)s type **IV** reported herein.

Outlook

During this work, the main focus was set on the synthesis of novel dinucleating ligands and their respective mono- and dinuclear metal complexes. Hereby, a multitude of dinuclear complexes bearing reactive sides was introduced, but their activity in catalytic transformations was only barely studied. Especially the heteroleptic complexes **XV**-**XVI** are assumed to exhibit an outstanding potential due to their versatility in metal centers as well as reactive groups. Additionally their tunable stereogenic center could make them suitable catalysts for stereoselective transformations.

Besides the catalytic application, also the isolation of an intramolecular magnesium dication based on the complex **Va** remains a challenging task for the future. Whereas a number of observations and spectroscopical measurements indicate the possible formation of the desired dications, crystallization and thus complete characterization could not be achieved so far.

References

[C1] (a) M. L. Hlavinka, J. R. Hagadorn, *Chem. Commun.*, **2003**, 2686; (b) M. L. Hlavinka, J. R. Hagadorn, *Organometallics*, **2005**, *24*, 5335.

8. Appendix

8.1 Thematic list of abbreviations

NMR spectroscopy

NMR	Nuclear magnetic resonance	t	triplet
δ	chemical shift	qu	quartet
ppm	Parts per million	quint	quintet
Hz	Hertz, s^{-1}	sept	septet
J	Coupling constant, Hz	m	multiplet
s	singlet	br	broad
d	doublet	VT	Variable-temperature

Cyclic voltammetry

CV	Cyclic voltammetry	µA	Microampere
Fc/Fc^+	Ferrocene/Ferrocenium	V	Volt

Solvents

THF	tetrahydrofuran	C_6H_5Cl	chlorobenzene
Et_2O	diethylether	C_6H_5Br	bromobenzene
DCM	dichloromethane		

General

^{t}Bu	*tert*-Butyl	T	Temperature [K]
^{i}Pr	*iso*-propyl	rt.	room temperature
Dipp	2,6-diisopropylphenyl	d	day
DMP	2,6-dimethylphenyl	h	hour
Mes	2,4,6-trimethylphenyl	ATR	Attenuated total reflection
Cy	cyclohexyl	IR	infrared
Ad	adamantane	ROP	Ring-opening polymerization
Me	methylene	Ae	alkaline-earth

et	ethylene
prop	propylene
but	butylene
xyl	xylylene
NacNac	β-diketimine
et al.	et alii
eq	equivalent
atm	standard atmosphere
His	histidine
Asp	aspartate
HOMO	highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital

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