Inorganic Chemistry

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# Synthesis and Coordination Chemistry of 3,4-Ethylene-Bridged 1,1,2,5-Tetrasubstituted Biguanides

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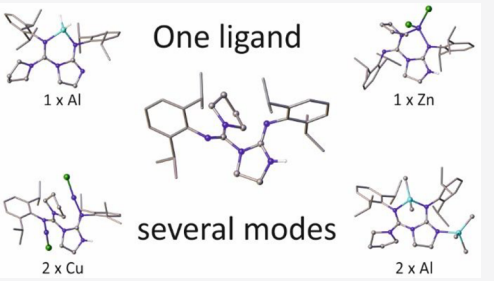
**ABSTRACT:** The synthesis of 3,4-ethylene-bridged 1,1,2,5-tetrasubstituted biguanides is reported, which are accessible by three alternative routes. Exemplary molecular structures of the ligand and an observed side product have been elucidated by X-ray diffraction analysis. Mono- and dinuclear complexes of the biguanide in both its neutral and monoanionic forms were obtained, including examples of aluminum, copper, magnesium, potassium, tin, and zinc, indicating a versatile coordination behavior, as evidenced by means of single-crystal X-ray diffraction analysis.






## INTRODUCTION

Biguanides **I** (Figure 1), which were already synthesized in 1879,[1] find numerous applications not only as ligands but also as important compounds in their own right: e.g., for the treatment of filariasis, hyperglycemia, influenza, and malaria,[2] with metformin (**II**) being the most prominent example. Surprisingly, in the case of the parent biguanide the wrong tautomer is regularly represented in the scientific literature.[3] While related metal complexes attracted quite some interest in the middle of the last century, reports faded after an initial period of intense research.[4] Recently, however, biguanide complexes have experienced a revitalization, as they have the potential to be large-spectrum antimicrobial and anticancer agents or catalysts for organic transformations.[5] However, the synthetic access to biguanides, especially to the more highly substituted derivatives, limits their applicability.[6] The synthesis of 1,1,2,4,5,5- or 1,2,3,4,5,5-hexasubstituted biguanides (**III**), for example, originating from carbodiimides is limited in terms of the substitution pattern and requires multiple steps.[7] However, a high degree of substitution is relevant in order to reduce the coordinational freedom, aiming to address the various requirements of a metal complex arising from the different areas of application such as catalysis, material design, and medicinal chemistry.

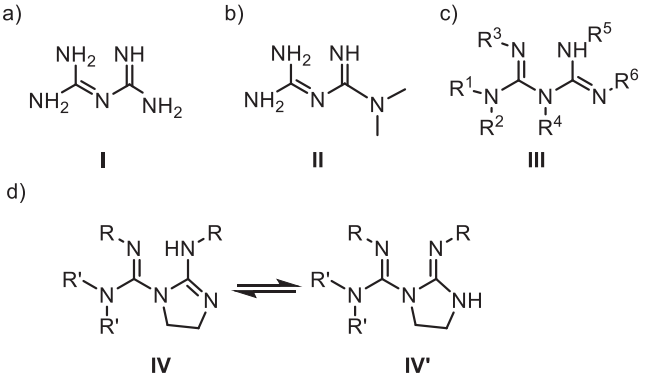



**Figure 1.** (a) The parent biguanide **I**, (b) the type 2 diabetes drug metformin **II**, and (c) 1,2,3,4,5,5-hexasubstituted biguanides. (d) The tautomeric forms of the 3,4-ethylene-bridged 1,1,2,5-tetrasubstituted biguanides presented in this work.

Due to our interest in polynuclear metal complexes, we became interested in bis(guanidines)[8] and developed a synthetic protocol to obtain these from readily available bis(thioureas).[9] However, when ethylene-bridged bis(thioureas) bearing terminal alkyl substituents were applied, we did not obtain the desired bis(guanidines). Instead, C−N bond scission takes place, yielding an isothiocyanate along with an N-substituted 4,5-dihydro-1*H*-imidazol-2-amine. However, when ethylene-bridged bis(thioureas) bearing bulky terminal aryl groups were used, 3,4-ethylene-bridged 1,1,2,5-tetrasubstituted biguanides were obtained in good yields along with the respective bis(guanidines) (vide infra). Inspired by these results, we set out to explore the synthetic access and coordination chemistry of this new ligand class, aiming for a comparison with the more classical biguanides. In comparison to the 1,2,3,4,5,5-hexasubstituted biguanides **III**, the five-membered heterocycle within **IV**/**IV′** gives rise to a more rigid ligand framework, which consequently will affect the coordination capabilities. However, the biguanides **IV**/**IV′**

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**Scheme 1. Synthetic Routes toward 3,4-Ethylene-Bridged 1,1,2,5-Tetrasubstituted Biguanides IV/IV′ from Readily Available Ethylene-Bridged Bis(thioureas) 1**

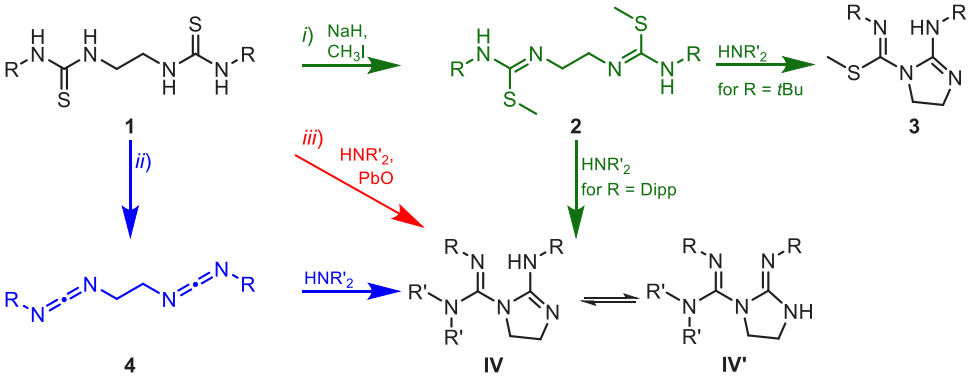
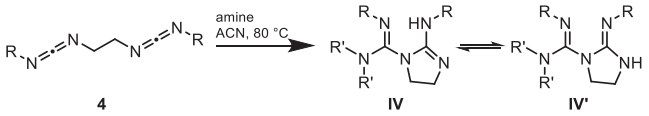



**Table 1. Synthesis of Biguanides IV/IV′ from Bis(carbodiimides) 4**




| entry | R | amine | yield (%) | entry | R | amine | yield (%) |
|---|---|---|---|---|---|---|---|
| 1 | Dipp | pyrrolidine | 61 (**IVa′**) | 6 | Dipp | piperidine | 35 (**IVf′**) |
| 2 | DMP | pyrrolidine | 62 (**IVb′**) | 7 | Dipp | azepane | 37 (**IVg′**) |
| 3 | phenyl | pyrrolidine | *a* | 8 | Dipp | diethylamine | nr |
| 4 | isopropyl | pyrrolidine | 41 (**IVc**) | 9 | Dipp | diisopropylamine | nr |
| 5 | *t*Bu | pyrrolidine | 58 (**IVd**) | 10 | Dipp | LDA | 18 (**IVh′**) |
| 6 | Dipp | morpholine | 42 (**IVe′**) | 11 | *t*Bu | LDA | 36 (**IVi**) |

[a]The protocol led to an intractable reaction mixture.

still offer multiple binding sites, and so we investigated the formation of certain coordination isomers depending on the metal applied in order to understand the coordination behavior. Furthermore, the substituents R and R′ can be varied independently, which allows for a fine tuning of the electronic properties of the ligand or for the introduction of suitable anchor and bridging groups in order to attach the ligand on surfaces or to connect several complexes, aiming for molecular assemblies.

## RESULTS AND DISCUSSION

**Proligand Synthesis and Structure.** We investigated three different approaches toward the biguanides **IV** or the respective tautomer **IV′** (Scheme 1), all originating from the bis(thioureas) **1**, which are readily available from ethylenediamine and the respective isothiocyanates. Route i is based on the formation of the respective S-methylated bis(isothioureas) **2**, for which the alkyl and aryl derivatives (R = *t*Bu, Dipp) are conveniently available by applying established protocols.[10] In the case of the terminal *tert*-butyl group, the reaction with pyrrolidine does not yield the desired biguanide. Instead, the N,N′-substituted *S*-methyl(4,5-dihydro-1*H*-imidazolyl-1)-isothiourea **3** is formed, which, to the best of our knowledge, has yet not been reported in the literature. However, if 2,6-diisopropylphenyl (Dipp) is used as the terminal substituent, the biguanide **IVa′** is formed in 37% yield.

Route ii involves the synthesis of the bis(carbodiimides) **4**, which have only limited precedence in the literature,[11] and the necessary distillative purification causes unwanted side reactions (such as polymerization reactions) for their heavier weight derivatives due to their higher boiling points. However, adopting procedures regularly used for the synthesis of carbodiimides[12] allowed for the isolation of alkyl- and aryl-substituted bis(carbodiimides) **4** in yields ranging from 23 to 63%. Bis(carbodiimides) bearing rather bulky terminal groups were accessible using cyanuric chloride as a desulfurization agent, while derivatives of **4** containing less bulky terminal groups, i.e., ethyl and phenyl, respectively, could only be obtained in low yields (23% and 28%, respectively) by using $PPh_3/Br_2$. The diminished yields in the latter case most likely arise from subsequent reactions such as polymerization and cyclopolymerization, which is a known behavior of poly(carbodiimides).[11a,13]

Treatment of the bis(carbodiimides) **4** with an excess of pyrrolidine allows for the isolation of the desired biguanides **IV** and **IV′**, respectively, in yields ranging from 35% to 62% (Table 1). It is worth noting that intramolecular reactions of protic groups and carbodiimides have already been observed: for example, in the formation of 2-amino-2-oxazolines.[14] Although the protocol tolerates terminal alkyl and 2,6-disubstituted aryl groups, the reaction of the phenyl-substituted bis(thiourea) gives rise to an intractable reaction mixture. With respect to the nucleophile, the reaction is limited to cyclic secondary amines, which is in line with the decreased nucleophilicity of acyclic secondary amines.[15] However, using the corresponding lithium amides is a suitable protocol to obtain the related biguanides (Table 1, entries 10 and 11). Using morpholine illustrates that bridging groups are readily installed in the backbone, as mentioned in the Introduction.

In order to elucidate which of the two tautomers, i.e., **IV** or **IV′** (Scheme 1) exists in solution, multidimensional NMR experiments have been conducted using **IVa′** and **IVi**,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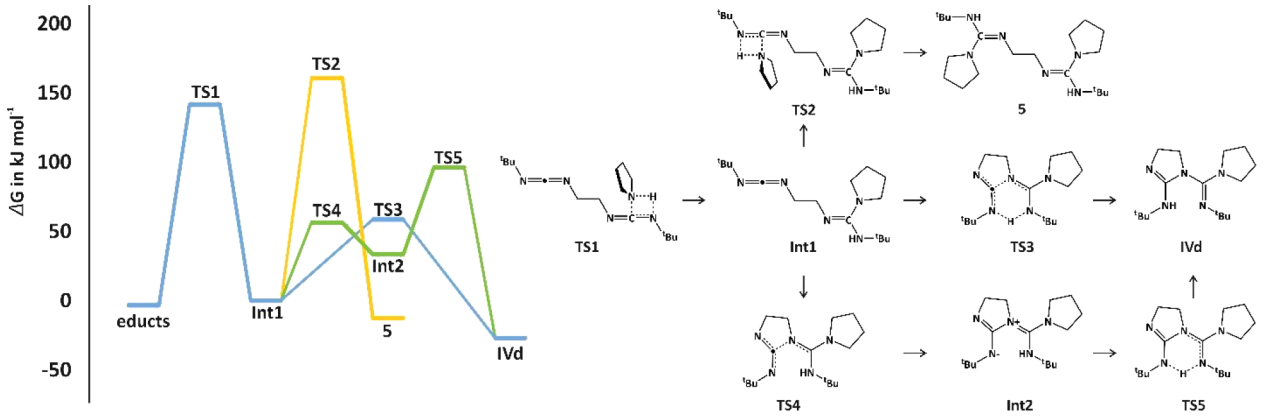
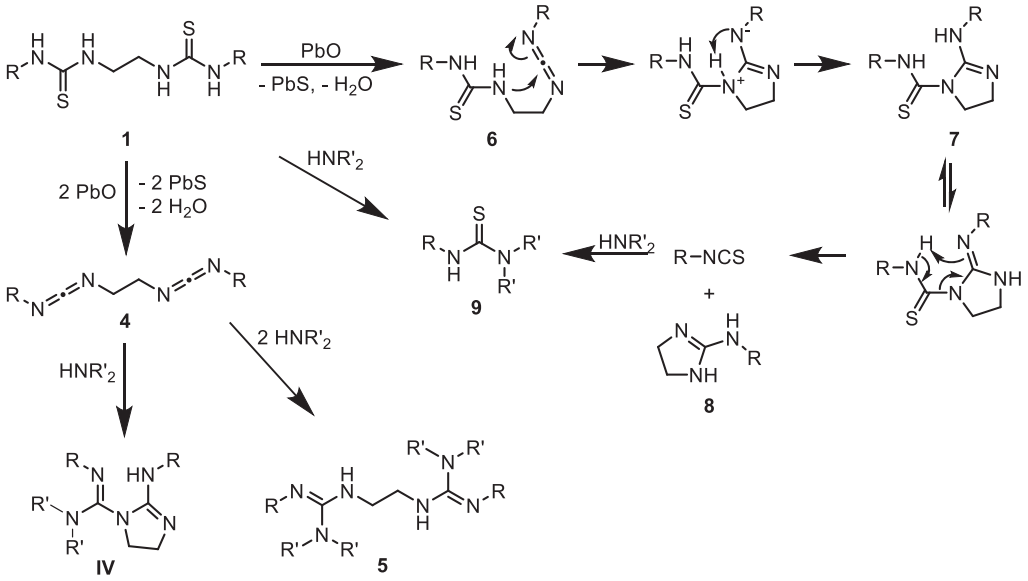



**Figure 2.** Possible reaction pathway and potential energy surface (Gibbs free energies at the B3LYP-D3/TZVP level of theory) for the reaction of the bis(carbodiimide) **4d** with pyrrolidine.

**Scheme 2. Possible Reaction Pathways Originating from the Bis(thioureas) 1 and Various Conditions**




respectively. Notably, for the known open chain biguanides no reports about the relationship between tautomer stability and substitution pattern can be found.[16] The N−H resonances appear in the $^{1}$H NMR spectrum as broad singlets at 3.82 (**IVa′**) and 3.83 (**IVi**) ppm. In the $^{1}$H,$^{1}$H-COSY NMR spectra in both cases only one cross peak was observed for these resonances (Figures S47 and S70, respectively). For **IVa′**, $^{3}J$ coupling with the triplet resonance at 3.36 ppm, which is assigned to the $CH_2$ group of the five-membered ring, was observed, while for **IVi** $^{4}J$ coupling to the singlet resonance at 1.20 ppm accounting for the *tert*-butyl group is observed. Furthermore, in the $^{1}$H,$^{13}$C-HMBC NMR spectrum of **IVa′**, a cross peak between the N−H and $^{13}$C methylene resonances at 47.2 ppm accounts for a $^{3}J$ coupling, while such a peak is absent in the case of **IVi**. Hence, evidence is given that in the case of **IVa′** the tautomer **IV′**, in which the proton is bound to the endocyclic nitrogen atom of the five-membered ring, is present in solution, while the data obtained for **IVi** carrying terminal *tert*-butyl groups are in favor of tautomer **IV**. This illustrates nicely the crucial effect of the terminal substituent, which is readily explained by the positive inductive effect of the alkyl group causing an increase in the basicity of the exocyclic nitrogen atom. In order to distinguish whether the biguanides exist as monomers or dimers formed through hydrogen bonding, diffusion ordered NMR spectroscopy (DOSY) experiments have been conducted using dioxane as an internal reference. The experimentally obtained hydrodynamic radii of **IVa′** (4.1 Å) and **IVi** (5.0 Å), respectively, are in good agreement with the calculated values (4.0−5.1 and 4.7−6.7 Å, respectively)[17] of the monomeric species.

DFT calculations at the B3LYP-D3/TZVP level of theory were performed to obtain mechanistic insights and to reveal the origin of the preferred formation of the biguanides **IV**/**IV′** over the formation of bis(guanidines) **5**. On the basis of the Gibbs free energies and as shown in Figure 2, formation of the biguanide **IVd** is favored by about 14.3 kJ mol$^{-1}$ over the related bis(guanidine). Notably, the also conceivable tautomer **IVd′** is 38.9 kJ mol$^{-1}$ higher in energy, in line with the experimental observation.

Initially, addition of pyrrolidine to **4d** favors the formation of a terminal rather than a lateral N−H bond, yielding the intermediate **Int1** via **TS1**; addition to the lateral C═N bond via transition state **TS1′** is 35.1 kJ mol$^{-1}$ higher in energy. From **Int1**, the reaction pathway branches out in three different reaction channels, which are discussed separately in the following. Addition of a second pyrrolidine molecule to


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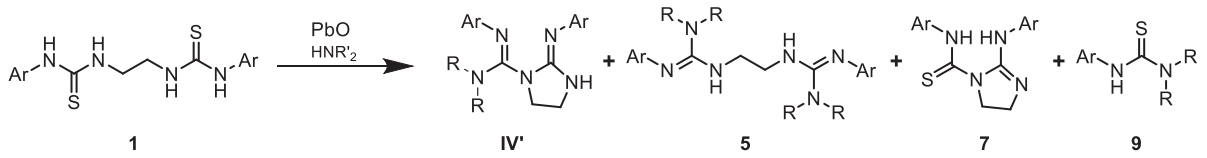
Table 2. Reactions of Bis(thioureas) 1 with Secondary Amines and Lead(II) Oxide[a]




1 IV' 5 7 9

| | | | yield (%) | | | |
|---|---|---|---|---|---|---|
| entry | Ar | amine | IV′ | 5 | 7 | 9 |
| 1 | Dipp | pyrrolidine | 60 (39) **IVa′** | 20 | 5 | 15 |
| 2 | DMP | pyrrolidine | 70 (46) **IVb′** | | | 30 |
| 3 | Dipp | morpholine | 30 (23) **IVe′** | | 10 | 50 |
| 4 | Dipp | piperidine | 90 (42) **IVf′** | | | |
| 5 | Dipp | azepane | 60 (37) **IVg′** | | | 20 |
| 6 | Dipp | diethylamine | | | 60 (44) | |
| 7 | 2-$CH_3$-$C_6H_4$ | pyrrolidine | | | | 99 (57) |
| 8 | 4-$CH_3$-$C_6H_4$ | pyrrolidine | | | | 99 (57) |
| 9 | 4-$NO_2$-$C_6H_4$ | pyrrolidine | | | | 75 (43)[b] |
| 10 | 4-F-$C_6H_4$ | pyrrolidine | [c] | | [c] | [c] |

[a]Crude yields were obtained from $^1$H NMR data, and isolated yields are given in parentheses. [b]In addition to compound **8h**, unreacted starting material was observed in the crude reaction mixture. [c]The protocol led to an intractable reaction mixture.

**Int1** proceeds via **TS2**, forming the respective bis(guanidine) **5**. Again, the proton transfer can occur either to the terminal or to the lateral nitrogen atom of the remaining carbodiimide unit, but in contrast to **TS1**, the respective transition states **TS2** and **TS2′** differ in energy by only 1.0 kJ mol$^{-1}$. However, thermodynamically, formation of **5** containing two terminal N−H bonds is favored by 11.6 kJ mol$^{-1}$ over the formation of **5′** containing a lateral and a terminal N−H bond.

For the biguanide formation, two pathways need to be considered: here, the nucleophilic attack of the lateral nitrogen atom of the guanidine unit to the electrophilic carbon atom of the carbodiimide unit and the proton transfer can occur in either a concerted reaction via **TS3** or by a subsequential process en route, **TS4** → **Int2** → **TS5**. However, and with respect to **Int1**, **TS3** (58.7 kJ mol$^{-1}$ relative to **Int1**) is much lower in energy in comparison to **TS2** (159.6 kJ mol$^{-1}$ relative to **Int1**) and **TS5** (95.9 kJ mol$^{-1}$ relative to Int1). Consequently, the sequence **TS1** → **Int1** → **TS3** → **IVd** belongs to the energetically preferred pathway for biguanide formation on route i. It is worth noting that the transition state **TS5′**, associated with the direct formation of the energetically less preferred tautomer **IVd′**, is 34.2 kJ mol$^{-1}$ more demanding in comparison to **TS5**.

Route iii, finally, is based on our previous work concerning the synthesis of bis(guanidines),[9] where we observed that the treatment of ethylene-1,2-bis(3-*tert*-butylthiourea) with PbO and pyrrolidine did not yield the desired bis(guanidine) but instead generated *N*-(*tert*-butyl)-4,5-dihydro-1*H*-imidazolyl-2-amine (**8**, R = C($CH_3$)$_3$). We assumed that the formation of **8** is most likely driven by the intermediary formation of the mixed carbodiimide thiourea species **6**, which undergoes an intramolecular cyclization, yielding the imidazolidyl carbothioamide **7** (Scheme 2). Subsequent C−N bond breakage gives rise to **8** and the intermediarily formed isothiocyanate reacts with an excess of pyrrolidine by generating the asymmetric thiourea **9**. Please note that symmetric N,*N*′-disubstituted thioureas are readily converted to the corresponding N,N′,N′-trisubstituted thioureas upon reaction with an excess of aliphatic or aromatic secondary amines.[18] Indeed, in a control experiment, **1g** was allowed to react with 20 equiv of pyrrolidine at 100 °C, leading to the isolation of **9** in 92% yield. Consequently, the desired formation of **4** competes with the generation of **6** and **9**, respectively.

Replacing the alkyl groups by electron-withdrawing aryl substituents should facilitate the desulfurization and thus suppress the formation of the mixed carbodiimide thiourea species **6**. Performing the reaction with ethylene-1,2-bis(2,6-diisopropylphenylthiourea) and ethylene-1,2-bis(2,6-dimethylphenylthiourea) allowed for the isolation of the desired biguanides **IVa′** and **IVb′** in 39% and 46% yield, respectively. However, the formation comes along with the generation of the imidazolidyl carbothioamide **7a** (R = Dipp) and of the asymmetric thiourea **9b** (R = 2,6-DMP, R′ = $(CH_2)_4$), respectively (Table 2). The protocol works with a variety of cyclic secondary amines, but the 2,6-substitution pattern of the terminal aryl groups appears to be most relevant, as the respective bis(thioureas) **1j**−**l**, bearing a 2-methylphenyl, 4-methylphenyl, or 4-nitrophenyl group, yield the N,N′,N′-trisubstituted thioureas **9** instead of the biguanide as the main product. Notably, the concentration is also crucial to the relative ratio of **IVa′** to **9a**: in low concentrations (0.05 mol/L of **1g**) **9a** was not observed in the crude product, while at a concentration of 0.16 mol/L, **9a** amounts to about 40% of the crude reaction mixture. Despite the fact that the reaction proceeds with various cyclic secondary amines, using acyclic diethylamine does not yield the desired biguanides but the imidazolidyl carbothioamide **7a** (R = Dipp) is formed as the major product (44% isolated yield) instead. Hence, applying bulky aryl groups stabilizes the species **7**, which was not detectable in the case of terminal *tert*-butyl groups.

In summary, the most relevant and sterically demanding biguanide **IVa′** can be obtained by three different routes, all originating from the readily available bis(thiourea) **1g**, from which the one-pot synthesis (route iii) is most preferred due to the facile workup. Route ii is the most versatile, as it also tolerates terminal alkyl substituents and allows the installation of acyclic secondary amines by applying the respective lithium amides.

Compounds **IVa′**, **IVb′**, and **7a** were obtained as single crystals suitable for X-ray diffraction studies, and their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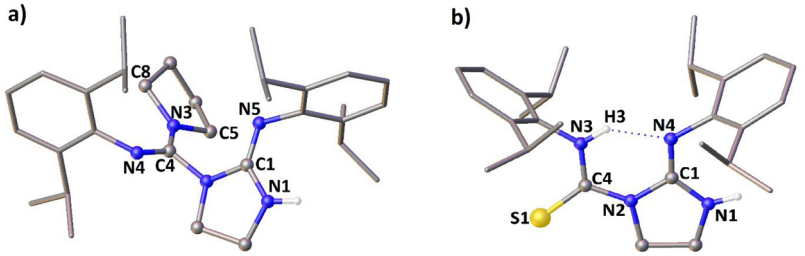
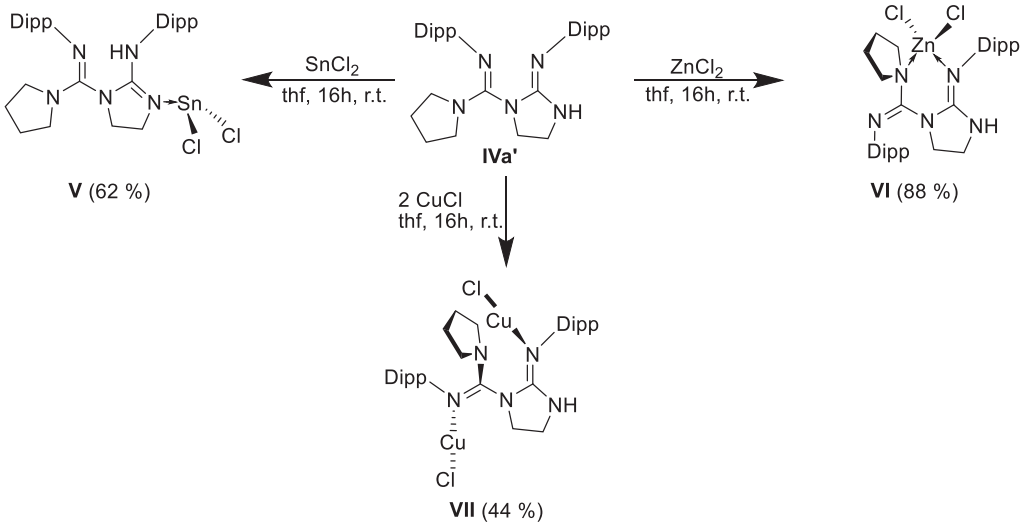



**Figure 3.** Solid-state structures (hydrogen atoms and for **7a** an acetonitrile molecule are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of **IVa′** and **7a**: (a) **IVa′**, C1−N1 1.3742(15), C4−N4 1.2778(15), C1−N5 1.2765(15), C5−N3−C8 111.33(10); (b) **7a**, C1−N1 1.347(3), C4−N3 1.339(3), N3−H3 0.91(3), C1−N4 1.283(3), C4−S1 1.673(2), N3−C4−S1 123.90(18), N2−C4−S1 121.24(18).

**Scheme 3. Synthesis of the Mononuclear Tin(II) and Zinc(II) Complexes V and VI, Respectively, and of the Diinuclear Copper(I) Complex VII Starting from the Protio Ligand IVa′**



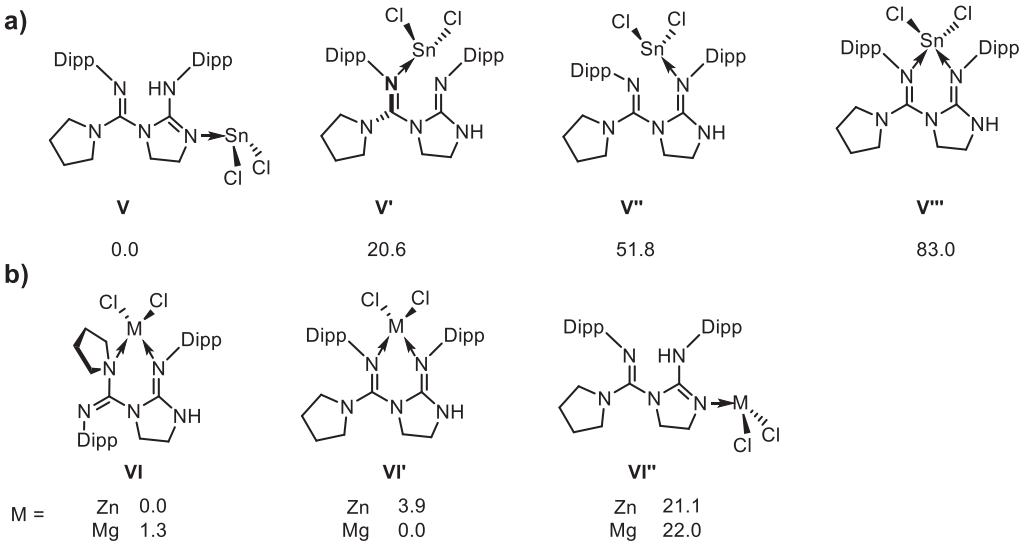




**Figure 4.** Relative Gibbs free energies (given in kJ $mol^{-1}$) of the isomers of (a) **V** and (b) **VI** and a hypothetical $MgCl_2$ complex at the B3LYP/def2SVP level of theory.

molecular structures are given in Figure 3 and Figure S1. As both **IVa′** and **IVb′** have similar structural features, further discussions are based solely on compound **IVa′**, for which also metal derivatives have been obtained (vide infra). However, the molecular structure in the solid state and selected bond lengths and angles of **IVb′** are given in Figure S1. The C1−N5 and C4−N4 bond lengths with values of 1.2765(15) and 1.27788(15) Å, respectively, are indicative of C=N double bonds. The C5−N3−C8 bond angle (111.33(10)°) of the pyrrolidine ring is more obtuse in comparison to free pyrrolidine (105.2(35)°).[19]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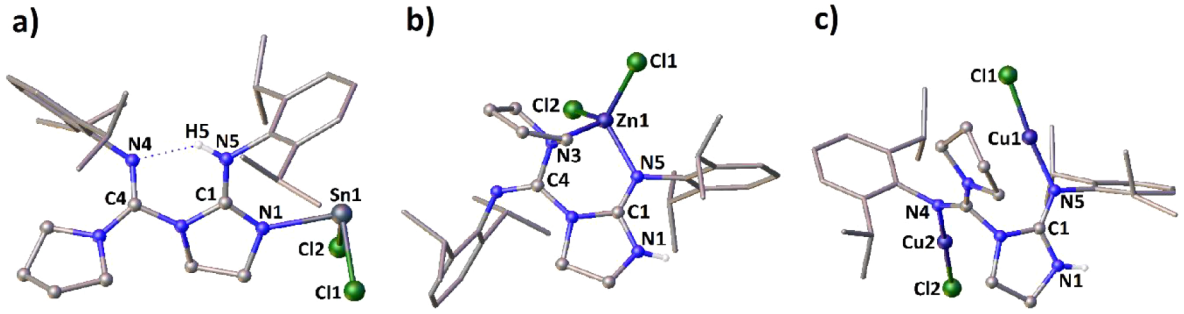


**Figure 5.** Solid-state structures (hydrogen atoms and in the case of **V** and **VI** residual toluene molecules are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of **V**–**VII**: (a) **V**, Sn1–N1 2.2216(17), Sn1–Cl1 2.4841(6), Sn1–Cl2 2.4647(5), C1–N1 1.314(3), C4–N4 1.285(3), C1–N5 1.337(2), N5–H5 0.86(3), N1–Sn1–Cl1 86.66(5), Cl1–Sn1–Cl2 94.88(2); (b) **VI**, Zn1–Cl1 2.2004(4), Zn1–Cl2 2.2135(4), Zn1–N5 1.9970(12), Zn1–N3 2.1455(11), C1–N1 1.3502(18), C1–N5 1.2968(18), C4–N3 1.4416(17), Cl1–Zn1–Cl2 115.016(16), N3–Zn1–N5 88.89(4); (c) **VII**, Cu1–Cl1 2.0929(7), Cu1–N5 1.872(2), Cu2–Cl2 2.0796(9), Cu2–N4 1.885(2), C1–N1 1.341(3), N5–Cu1–Cl1 174.72(6), N4–Cu2–Cl2 173.06(7).

Compound **7a** carries two nitrogen-based protons at N1 and N3, respectively. This causes the formation of an intramolecular N3–H3···N4 hydrogen bond, generating a pseudobicyclic framework. Consequently, the C1–N1 bond in **7a** (1.347(3) Å) is significantly shorter in comparison to that in **IVa′** (1.3742(15) Å). The $^1$H NMR spectrum of **7a** gives a pattern of two methine septets and four methyl doublets for the Dipp groups, which is indicative of a plane of symmetry within the molecule, and the two N–H resonances appear as broad singlets at 4.34 and 13.43 ppm, respectively.

**Complexation Behavior.** Having the related protio ligands in hand, we set out to investigate their coordination capabilities of both the neutral and monoanionic forms and chose biguanide **IVa′** as a reference compound. Due to the anti-infective properties and large antimicrobial spectrum of biguanide complexes of the middle and late 3d metals,[5a] we chose copper and zinc as examples along with tin as a representative of a main-group element. Under anaerobic conditions **IVa′** readily forms the complexes **V**–**VII** upon treatment with $SnCl_2$, $ZnCl_2$, and CuCl, respectively (Scheme 3). Their molecular structures in the solid state are given in Figure 5. Addition of $SnCl_2$ to **IVa′** induces a proton transfer from N1 to N5, giving rise to an intramolecular N4···H5–N5 hydrogen bond along with the formation of a pseudobicyclic ring system. $SnCl_2$ coordinates to the endocyclic N1 atom occupying the apex of the trigonal pyramid. The formation of only one dative N–Sn bond instead of formation of a chelate was also observed in the case of an acenaphthene-1,2-diimine, for which, however, a substantially longer coordinative Sn–N bond (2.4700(7) Å) in comparison to **V** (2.2216(17) Å) has been reported. In the case of **VI**, the zinc atom is not bound to both imine moieties but instead to the nitrogen atoms of the amino (N3) and imino function (N5). Consequently, the Zn–N bond lengths of 1.9970(12) Å (Zn1–N5) and 2.1455(11) Å (Zn1–N3) resemble those observed for aminoimine zinc complexes.[20] This stands in contrast to the well-known NacNac ligand, for which the related unfavorable $\beta$-diimine form is stabilized in the coordination sphere of divalent metals such as $NiBr_2$[21] and $ZnCl_2$.[22]

While the $^1$H NMR spectrum of **V** gives sharp signals, which indicate $C_s$ symmetry on the NMR time scale, broadened resonances attributed to slow conformational exchange at room temperature were observed for compound **VI**. By acquisition of the spectra at 233 K the majority of the resonances were resolved and allowed their assignment to individual protons within the complex, although the resonances remained comparably broad (Figures S81–S84). It is worth noting that the limited solubility of **VI** in solvents other than $CDCl_3$ impedes the acquisition of spectra at elevated temperature.

Aiming to obtain insight into the different binding scenarios, we performed DFT calculations at the B3LYP/def2SVP level of theory for the conceivable isomers of **V**, **VI**, and a hypothetical $MgCl_2$ complex of **IVa′** (Figure 4). In the case of the tin(II) complex, **V** belongs to the most stable isomer and **V′**, **V′′**, and **V′′′** are higher in energy by 20.6, 51.8, and 83.0 kJ mol$^{-1}$, respectively. Steric demands are likely to account for this significant energy difference, as in the case of **V′** and **V′′** the interaction of the $SnCl_2$ fragment with the bulky Dipp groups is more pronounced in comparison to **V**. In **V′′′**, finally, the tin center adopts a seesaw geometry, which is less favored due to obvious electronic reasons. The relative energies of the isomers of both the zinc(II) and the respective hypothetical magnesium(II) complex (Figure 4b) indicate an opposite behavior, as **VI′′** is the least favored isomer. The isomers **VI** and **VI′** with M being Mg and Zn differ only slightly in energy, and in line with the experiment, **VI** is the most stable isomer in the case of zinc, while for magnesium **VI′** is slightly lower in energy by 1.3 kJ mol$^{-1}$. This indicates that even relatively "cheap" basis sets allow for a prediction of the coordination geometry, which is of value for further application of the biguanides **IV**/**IV′** as ligands.

In the case of copper(I), the dinuclear complex **VII** is obtained in which the two CuCl units are each $\kappa^1$-bound to N4 and N5, respectively. It is worth noting that **VII** is formed independently from the stoichiometry of **IVa′** to CuCl and using a 1:1 ratio yields the dinuclear complex **VII** along with unreacted protio ligand. The overall structure of **VII** is reminiscent of the dinuclear copper(I) methanetrisamidine complex reported by the Schulz group[23] and hence features similar structural characteristics. Each CuCl molecule is $\kappa N^1$-coordinated by one of the two imino groups, while the N–H bond at N1 remains intact. The Cu–N bond lengths (Cu1–N5 1.872(2) Å, Cu2–N4 1.885(2) Å) and the N–Cu–Cl bond angles (N5–Cu1–Cl1 174.72(6)°, N4–Cu2–Cl2 173.06(7)°) are comparable to those observed by Schulz and co-workers.[23] Coordination of the Lewis acidic CuCl molecules causes a flux of electron density from the nitrogen atoms to the copper ions; therefore, the C1–N5 (1.310(3) Å) and C4–N4 (1.301(4) Å) bonds are elongated in comparison


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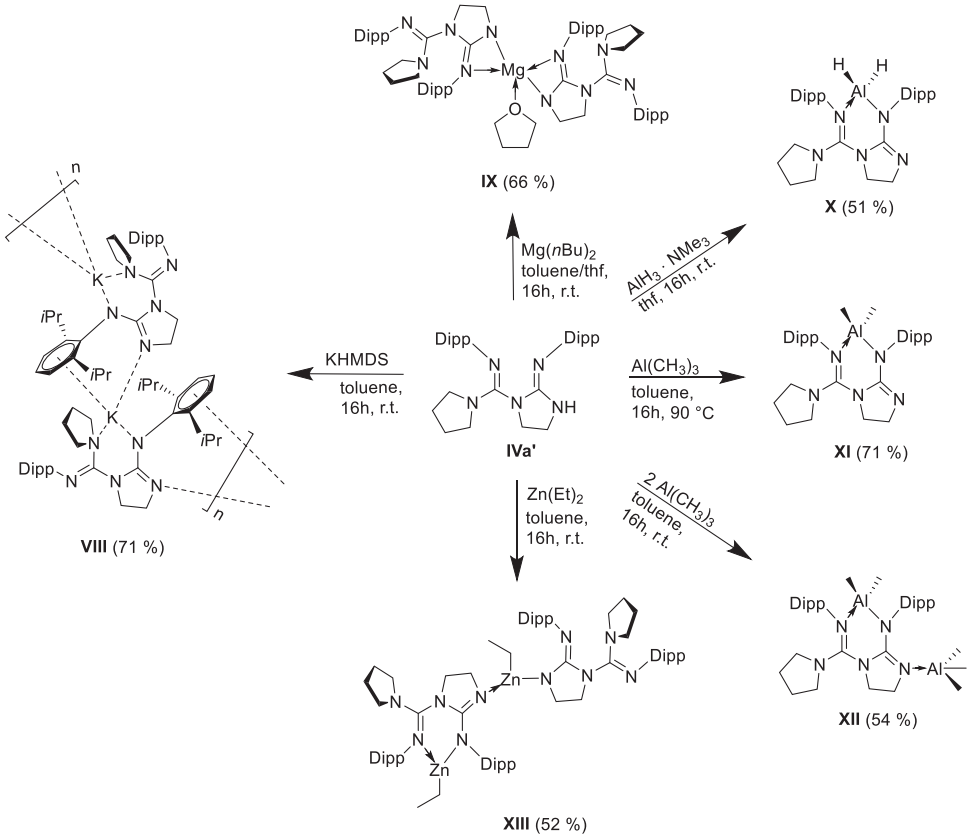
**Scheme 4. Synthesis of the Potassium, Magnesium, Aluminum, and Zinc Complexes VIII–XIII Originating from the Protio Ligand IVa′**



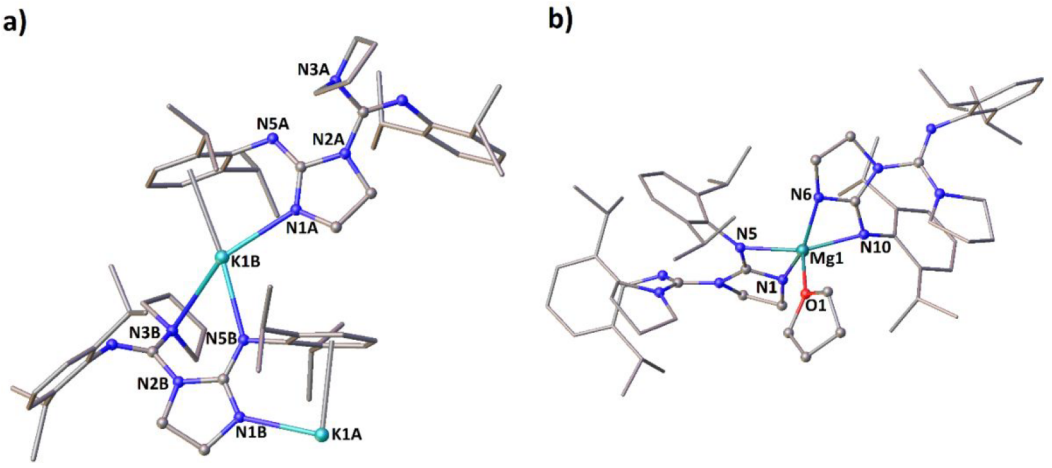




**Figure 6.** Solid-state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg): (a) **VIII**, K1B–N1A 2.733(5), K1B–N3B 3.113(5), K1B–N5B 2.666(5), K1B–RING 2.938(5), N3B–K1B–N5B 61.90(14), N1A–K1B–N5B 105.23(16); (b) **IX**, Mg1–N1 2.0787(17), Mg1–N5 2.1437(17), Mg1–N6 2.0791(18), Mg1–N10 2.1592(15), N1–Mg1–N5 64.80(6), N6–Mg1–N10 64.66(6).

to the protio ligand **IVa′** (1.2765(15) and 1.2778(15) Å, respectively). Notably, copper complexes of the more traditional and less substituted biguanide ligands are also known and regularly incorporate copper(II) centers chelated by two biguanides.[5a,24] Obviously, the bulky Dipp groups of **IVa′** would inhibit the formation of a comparable mononuclear copper complex.

The $^{1}$H and $^{13}$C NMR spectra of **VII** in $CDCl_3$ are consistent with the solid-state structure on the NMR time scale and provide well-resolved resonances. The $^{1}$H NMR spectrum includes two sets of two doublets for the methyl groups of each Dipp substituent, originating from a hindered rotation about the $C_{aryl}$–N bonds. In addition, the NH resonance appears at lower field (8.89 ppm) in the $^{1}$H NMR in comparison to the protio ligand **IVa′**. Overall, the three complexes reported before nicely illustrate that each tautomer, i.e., **IVa** and **IVa′**, can be stabilized by selecting the proper metal.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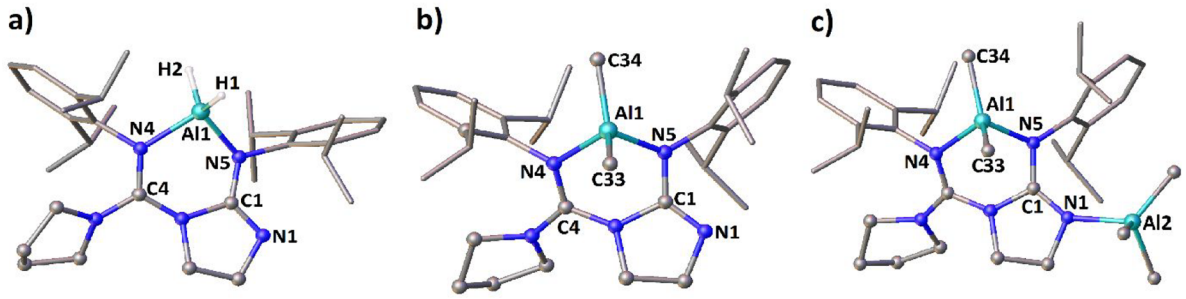


**Figure 7.** Solid-state structures (hydrogen atoms are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg): (a) **X**, Al1−N4 1.9210(12), Al1−N5 1.8590(12), C1−N1 1.2756(19), C1−N5 1.3490(18), N4−Al1−N5 95.69(5), H1−Al1−H2 111.8(10);( b) **XI**, Al1−N4 1.9477(11), Al1−N5 1.8966(11), C1−N1 1.2847(16), C1−N5 1.3567(16), N4−Al1−N5 94.23(5), C33−Al1−C34 120.26(6); (c) **XII**, Al1−N4 1.9460(11), Al1−N5 1.9385(11), C1−N1 1.3194(15), C1−N5 1.3415(15), Al2−N1 1.9937(11), N4−Al1−N5 93.91(4), C33−Al1−C34 122.31(6).

In addition to complexes **V**−**VII**, in which the neutral protio ligand remains present, deprotonation is readily achieved using potassium bis(trimethylsilyl)amide (KHMDS), di-*n*-butylmagnesium, aluminum hydride trimethylamine complex, trimethylaluminum, and diethylzinc, giving rise to manifold coordination modes (Scheme 4 and Figures 6−8). The elements have been chosen because of the potential application of the related product. The potassium species may act as a precursor for transmetalation or salt metathesis. However, the aluminum, magnesium, and zinc complexes are of potential interest for catalytic applications such as the Meerwein−Ponndorf−Verley reaction, as reported before for aluminum biguanide complexes.[5f]

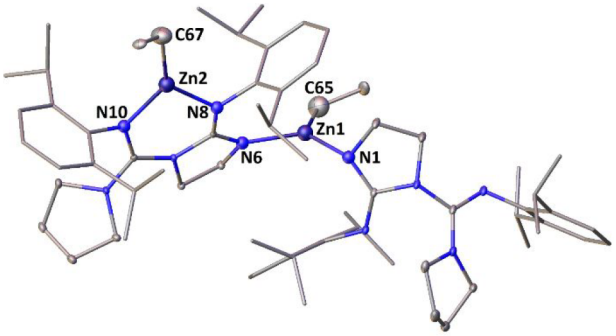


**Figure 8.** Solid-state structure (hydrogen atoms and residual pentane molecule are omitted for the sake of clarity) with selected bond lengths (Å) and angles (deg) of **XIII**: Zn1−N1 1.945(2), Zn1−N6 1.995(2), Zn2−N8 1.962(2), Zn2−N10 1.987(2), Zn1−C65 1.988(3), Zn2−C67 1.955(3), N1−Zn1−N6 119.07(10), N8−Zn2−N10 95.11(8).

The potassium species **VIII** forms a 1D coordination polymer network[25] in the solid state, in which the anionic ligand provides four donor sites (Figure 6a and Figure S2). Each potassium coordinates in a $\kappa^2$ mode to the nitrogen atoms N3 and N5 of one ligand molecule and in a $\kappa^1$ and $\eta^6$ fashion to both the nitrogen atom N1 and the phenyl ring of the Dipp group bound to N5. So far, there has been only one report about such a $\kappa N^2$-$\kappa N^1$,$\eta^6$-binding behavior, which was observed for a multidentate nitrogen−sulfur ligand that, however, does not give rise to a coordination polymer but forms a dimer in the solid state.[26] The potassium bond lengths are in the range of 2.666(5) Å (K1B−N5B) to 3.113(5) Å (K1B−N3B), and the distance of the potassium ion to the center of the C6 perimeter (2.938 Å) is in the expected range.[27]

The $^1$H NMR spectrum of a solution of **VIII** in $d_8$-THF measured at room temperature contains well-resolved and assignable signals (Figure S87), while certain resonances appeared broad in the respective $^{13}$C spectrum. Upon cooling to 223 K, the $^{13}$C resonances became more sharp, while in the case of the $^1$H NMR spectrum a temperature dependence of the chemical shift, line broadening, and the eventual splitting of certain signals was observed (Figures S92−S94). With respect to the latter, the $^1$H resonances of the methylene groups of the pyrrolidine ring, for example, now appear as four broad singlets in comparison to two singlets at room temperature, indicating the inhibition of ring inversion upon cooling.

In case of compound **IX**, magnesium does not form a six-membered chelate ring but instead coordination originates from the nitrogen atoms N1 and N5 of two ligands, forming a spiro[3.3] compound in which the magnesium atom fuses two four-membered rings and reaches a coordination number of 5 upon complexation of a THF molecule. The formation of **IX** is in line with the propensity of heteroleptic alkaline-earth-metal complexes of the general formula LMX to undergo a Schlenk-like solution redistribution to the respective homoleptic compounds $L_2M$ along with $MX_2$. Such a coordination mode has previously been observed for amidinate[28] and guanidinate[29] complexes, and the magnesium−nitrogen bond lengths of 2.0787(17) Å (Mg1−N1) to 2.1592(15) Å (Mg1−N10) and N−Mg−N bond angles of 64.66(6)° (N6−Mg1−N10) to 64.80(6)° (N1−Mg1−N5) are in accordance with those reported before.

Due to the rotational dynamics of **IX** at room temperature, it was not possible to derive $^1$H and $^{13}$C spectra that allowed for an assignment of the signals and additional NMR experiments were conducted at 223 and 334 K (Figures S102−S111). Across the investigated temperature range, a pronounced temperature dependence of the chemical shifts was observed. On acquisition of the $^1$H NMR spectrum at 223 K, the rate of exchange was sufficiently reduced; thus, the majority of resonances were resolved. However, the slow exchange caused sufficiently more complex spectra. At 343 K an expected fast exchange caused a $^1$H NMR spectrum containing well-resolved but averaged resonances, which could be assigned to individual protons of complex **IX**.

Reaction of the protio ligand **IVa** with 1 equiv of aluminum hydride trimethylamine complex or trimethylaluminum readily


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affords the mononuclear species **X** and **XI** in 51% and 71% yields, respectively (Scheme 4). Notably, in case of compound **XI** the reaction conditions are crucial, as the reaction with 1 equiv of trimethylaluminum at room temperature yields the dinuclear species **XII** along with unreacted starting material. In **X** and **XI**, the biguanide chelates the aluminum atom, forming a nonplanar six-membered $AlC_2N_3$ ring, similar to those complexes obtained with NacNac and closely related ligands.[30] Their NMR spectroscopic data as well as the characteristics of their solid-state structures differ to quite some extent, as delocalization cannot be achieved within **X** and **XI**. Common features observed in the respective $^1$H NMR spectra include four doublets for the methyl groups and two septets for the methine groups of the Dipp ligand, indicating an averaged $C_s$ symmetry on the NMR time scale. In the case of **XI**, further evidence is given by one singlet at −0.93 ppm related to the $Al(CH_3)_2$ methyl group. In the solid state, the Al1−N5 bonds (1.8590(12) and 1.8966(11) Å for **X** and **XI**, respectively) are shorter in comparison to the Al1−N4 bonds (1.9210(12) and 1.9477(11) Å for **X** and **XI**, respectively) due to the covalent character of the former. The longer Al−N bonds and the hence more acute N4−Al−N5 bond angle of 94.23(5)° for **XI** in comparison to **X** (95.69(5)°) accounts for the reduced electron-withdrawing character of the methyl versus the hydride substituent. Short C1−N1 and C4−N4 bond lengths are in agreement with localized carbon−nitrogen double bonds. For **X**, the presence of an $AlH_2$ group was established by IR and $^1$H NMR spectroscopy: the asymmetric and symmetric Al−H stretches occur at 1802 and 1833 $cm^{-1}$, and the mean value of 1823 $cm^{-1}$ is blue-shifted in comparison to the respective complexes incorporating the NacNac ligand or its electron-rich derivative with mean values of 1814 and 1817 $cm^{-1}$, respectively.[31]

Upon coordination of an additional $Al(CH_3)_3$ molecule, the dinuclear species **XII** is formed, which resembles structural features of the dinuclear bicyclic aluminum derivatives obtained by the Schulz group from the reaction of propylene- and butylene-bridged bis(carbodiimides) with trimethyl aluminum at elevated temperatures.[11b] In comparison with **XI**, the Al1−N4 bond remains unaffected within the experimental error but the bonds associated with N1, C1, and N5 are elongated due to the Lewis acidic nature of Al2. The $^1$H NMR spectrum of **XII** contains distinct resonances for the methyl groups of the bridging (Al1) and terminal (Al2) aluminum centers at −0.93 and −1.36 ppm, respectively. While the latter appears as a sharp singlet, indicating free rotation about the Al2−C and Al2−N1 bonds, the former is broad due to hindered rotation about the Al1−C bonds, which is in contrast with the results obtained for **XI**, where one sharp singlet at −0.93 ppm was observed. In the $^{27}$Al NMR spectra of the compounds **X**−**XII**, no signals were detectable.

Finally, the protio ligand **IVa** was reacted with diethylzinc at −78 and 90 °C, yielding in both cases colorless crystals after a short workup. The $^1$H NMR spectra are identical for both fractions and have a complex pattern of resonances, whose origin has been elucidated by means of single-crystal X-ray diffraction (Figure 8). While one zinc atom (Zn2) is chelated by the two Dipp-substituted nitrogen atoms N8 and N10, forming a nonplanar six-membered $ZnC_2N_3$ ring, similarly to compounds **X** and **XI**, a second zinc (Zn1) is acting as a bridge to a second deprotonated ligand molecule in a nonchelating fashion. Overall, the dinuclear complex **XIII** consisting of two anionic ligand molecules and two zinc ions with a coordination number of 3 is obtained. The Zn−C bond lengths of 1.955(3) and 1.988(3) Å for Zn2−C67 and Zn1−C65, respectively, are comparable to those obtained for the related NacNac derivatives.[32]

## CONCLUSION

In summary, the synthesis of a new class of electron-rich N,N-bidentate ligands, i.e. 3,4-ethylene-bridged 1,1,2,5-tetrasubstituted biguanides, is reported, incorporating three synthetic methodologies originating from readily available bis(thiourea)s. Although the most relevant biguanide **IVa′** is obtained by each of the three routes, the one-pot synthesis (route iii) is preferred over the others due to the facile workup. However, the most versatile route ii also tolerates terminal alkyl substituents and allows the installation of acyclic secondary amines to the backbone of the ligand. The protio ligand **IVa′** readily forms complexes upon reaction with $SnCl_2$, $ZnCl_2$, or CuCl, in which the proton resides either on the endocyclic nitrogen atom N1 (Cu, Zn) or on the acyclic N5 position (Sn). Deprotonation of the protio ligand by using potassium bis(trimethylsilyl)amide (KHMDS), di-*n*-butylmagnesium, aluminum hydride trimethylamine complex, trimethylaluminum, and diethylzinc is readily achieved. In the case of potassium a 1D coordination polymer is obtained, which might serve as a suitable precursor in subsequent transmetalation reactions. While the Schlenk equilibrium favors the formation of a homoleptic magnesium complex, with $AlH_3{\cdot}N(CH_3)_3$ and trimethylaluminum mono- and dinuclear heteroleptic complexes are obtained, which will be further tested in catalytic applications. Finally, diethylzinc gives rise to a heterodinuclear zinc complex incorporating two ligand molecules. Although the coordination chemistry does not seem trivial, preliminary DFT calculations indicate that a prediction of the coordination geometry is feasible.

## EXPERIMENTAL SECTION

Further details on the synthesis of the protio ligands are given in the Supporting Information.

**General Procedure for the Synthesis of Bis(carbodiimides) 4.** A suspension of the bis(thiourea) **1** (3.0 mmol) and triethylamine (6.00 g, 60 mmol) in 25 mL of dichloromethane was cooled with an ice bath and treated with cyanuric chloride (2.22 g, 12 mmol). After 15 min 50 mL of petroleum ether was added to the yellow-orange mixture and stirring was continued for an additional 5 min. The solids were filtered off, and the gray residue was washed with 25 mL of petroleum ether. The combined filtrates were concentrated in vacuo, and the resulting mixture was suspended in 15 mL of *n*-pentane and filtered over Celite. The filter cake was washed with 5 mL of *n*-pentane, and the combined filtrates were concentrated in vacuo, giving the desired bis(carbodiimides) **4** as oily liquids pure enough for subsequent reactions.

***4a***. Yellow oil, 63%. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 24H, $CH_3$) 3.37 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.61 (br, 4H, $N(CH_2)_2N$), 7.12 (br, 6H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 23.3 ($CHCH_3$), 29.1 ($CHCH_3$), 47.7 ($N(CH_2)_2N$), 123.2 (*m*-$CH_{arom}$), 125.0 (*p*-$CH_{arom}$), 132.9 (NCN), 133.8 (*o*-$C_{arom}$), 142.4 (*i*-$C_{arom}$). IR ($cm^{-1}$): $\nu$(NCN) 2130, $\nu$(CN) 1659.

**General Procedure for the Synthesis of Biguanides IV from Bis(carbodiimides) 4.** A mixture of the bis(carbodiimide) **4** (1.5 mmol) and pyrrolidine (2.13 g, 30.0 mmol) in 40 mL of acetonitrile was stirred at 80 °C for 16 h. After it was cooled to room temperature, the solution was concentrated in vacuo. The residue was dissolved in hot acetonitrile, cooled to room temperature, and stored at −28 °C, causing crystallization of the desired biguanide.

**General Procedure for the Synthesis of Biguanides IV/IV′ from Bis(thioureas) 1.** A mixture of the bis(thiourea) **1** (1.0 mmol),


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1.42 g (20.0 mmol) of pyrrolidine, and 0.45 g (2.1 mmol) of PbO in 40 mL of toluene was stirred at 100 °C for 16 h. After the mixture was cooled to room temperature, the solids were filtered off and washed with toluene and the combined filtrates were concentrated in vacuo. The obtained residue was dissolved in hot acetonitrile, and the desired product was crystallized at −28 °C.

***IVa′***. Colorless blocks, 39%, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.17 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.65 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.19 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C$H$CH$_3$), 3.25 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.36 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $NCH_2CH_2NHC$), 3.83 (br, 1H, $NCH_2CH_2NHC$), 3.95 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $NCH_2CH_2NHC$), 6.94 (t, $^3J_{HH}$ = 7.2 Hz, 1H, $p$-C$H_{arom}$), 6.98 (t, $^3J_{HH}$ = 7.2 Hz, 1H, $p$-C$H_{arom}$), 7.04 (d, $^3J_{HH}$ = 7.2 Hz, 2H, $m$-C$H_{arom}$), 7.11 (d, $^3J_{HH}$ = 7.1 Hz, 2H, $m$-C$H_{arom}$). $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): $\delta$ 22.5 (CHC$H_3$), 23.6 (CHC$H_3$), 23.7 (CHC$H_3$), 23.8 (CHC$H_3$), 25.3 ($CH_2(CH_2)_2CH_2$), 28.1 (CHC$H_3$), 28.2 (CHC$H_3$), 40.0 ($NCH_2CH_2NHC$), 47.2 ($NCH_2CH_2NHC$), 48.0 ($CH_2(CH_2)_2CH_2$), 121.2 ($p$-C$H_{arom}$), 122.1 ($m$-C$H_{arom}$), 122.4 ($p$-C$H_{arom}$), 123.1 ($m$-C$H_{arom}$), 138.4 ($o$-$C_{arom}$), 140.2 ($o$-$C_{arom}$), 144.5 ($i$-$C_{arom}$), 145.3 ($i$-$C_{arom}$), 145.6 ($N_{pyrrolidine}$CNDipp), 151.4 (NHCNDipp). IR (cm$^{-1}$): $\nu$(NH) 3427, $\nu$(CH$_3$) 2956, $\nu$(CN) = 1672, $\nu$(CC$_{arom}$) 1639, 1585, and 1483. HR-ESI-MS: calcd for $C_{32}H_{47}N_5$ [M + H]$^+$ 502.3910; found 502.3903. Anal. Calcd for $C_{32}H_{47}N_5$: C, 76.60; H, 9.44; N, 13.96. Found: C, 76.68; H, 9.49; N, 13.85.

**Synthesis of the Metal Complexes V−XIII.** ***V***. A mixture of 0.50 g (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)imidazolidinyl-2-imine and 0.21 g (1.1 mmol) of $SnCl_2$ in 10 mL of tetrahydrofuran was stirred at room temperature for 16 h. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was dissolved in toluene, and the desired product **V** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.43 g, 0.6 mmol, 62%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.77 (quint, $^3J_{HH}$ = 3.3 Hz, 4H, $CH_2(CH_2)_2CH_2$), 3.04−3.17 (m, 4H, $CH_2(CH_2)_2CH_2$), 3.11 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C$H$CH$_3$), 3.94 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $NCH_2CH_2N$=C), 4.19 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $NCH_2CH_2N$=C), 7.02−7.08 (m, 3H, C$H_{arom}$), 7.27 (d, $^3J_{HH}$ = 7.7 Hz, 2H, $m$-C$H_{arom}$), 7.34 (t, $^3J_{HH}$ = 7.7 Hz, 1H, $p$-C$H_{arom}$), 9.70 (br, 1H, N$H$). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$): $\delta$ 22.7 (CHC$H_3$), 23.1 (CHC$H_3$), 24.7 (CHC$H_3$), 24.9 (CHC$H_3$), 25.5 ($CH_2(CH_2)_2CH_2$), 28.5 (C$H$CH$_3$), 28.9 (C$H$CH$_3$), 45.7 ($CNCH_2CH_2N$=C), 49.1 ($CH_2(CH_2)_2CH_2$), 50.1 ($CNCH_2CH_2N$=C), 122.9 ($m$-C$H_{arom}$), 123.8 ($p$-C$H_{arom}$), 126.0 ($m$-C$H_{arom}$), 130.4 ($p$-C$H_{arom}$), 131.7 ($i$-$C_{arom}$), 139.0 ($o$-$C_{arom}$), 141.6 ($o$-$C_{arom}$), 145.7 ($N_{pyrrolidine}$CNDipp), 146.9 ($i$-$C_{arom}$), 160.7 (N=CNDipp), $^{119}$Sn NMR (199 MHz, $CDCl_3$): $\delta$ −178.7. Anal. Calcd for $C_{32}H_{47}Cl_2N_5Sn$: C, 55.59; H, 6.85; N, 10.13. Found: C, 55.80, H, 6.95, N, 10.12.

***VI***. A 0.50 g portion (1.0 mmol) of(*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)-imidazolidinyl-2-imine was dissolved in 20 mL of tetrahydrofuran. Also, 0.14 g (1 mmol) of $ZnCl_2$ was dissolved in another Schlenk. Then the solution of the biguanide-based ligand system was added to the $ZnCl_2$ solution. Immediately after the addition a white suspension could be observed. The reaction mixture was stirred for 16 h. The mixture was concentrated in vacuo. The white solid was taken up in hot toluene (100 mL). The product **VI** was crystallized in the form of colorless blocks at room temperature after a few minutes. Colorless crystals, 0.56 g, 0.9 mmol, 88%. $^1$H NMR (400 MHz, $CDCl_3$, room temperature): $\delta$ 1.15 (br, 6H, CHC$H_3$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.29 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.73 (br,4H, $CH_2(CH_2)_2CH_2$), 2.94 (br, 4H, C$H$CH$_3$), 3.35 (br, 2H, $CNCH_2CH_2NH$), 3.54 (br, 4H, $CH_2(CH_2)_2CH_2$), 4.09 (br, 2H, $CNCH_2CH_2NH$), 4.77 (br, 1H, N$H$), 7.13−7.28 (m, 6H, C$H_{arom}$). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$, room temperature): $\delta$ 23.4 (CHC$H_3$), 24.1 ($CH_2(CH_2)_2CH_2$), 24.6 (CHC$H_3$), 25.1 (C$H$CH$_3$), 26.2 (CHC$H_3$), 28.0 (C$H$CH$_3$), 28.4 (CHC$H_3$), 39.7 ($CNCH_2CH_2NCH$), 49.6 ($CH_2(CH_2)_2CH_2$), 53.5 ($CNCH_2CH_2NH$), 123.6 ($CH_{arom}$), 124.8 ($CH_{arom}$), 126.7 ($CH_{arom}$), 137.5 ($C_{arom}$), 139.0 ($C_{arom}$), 142.5 ($C_{arom}$), 143.4 ($C_{arom}$), 150.0 ($N_{pyrrolidine}$CNDipp), 157.6 (N=CNDipp), $^1$H NMR (400 MHz, $CDCl_3$, −40 °C (233 K)): $\delta$ 1.04 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.65 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.18 (br, 4H, C$H$CH$_3$), 3.32 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $CNCH_2CH_2NH$), 3.49 (br, 4H, $CH_2(CH_2)_2CH_2$), 4.06 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $CNCH_2CH_2NH$), 4.86 (br, 1H, N$H$), 7.08−7.28 (m, 6H, C$H_{arom}$). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$, −40 °C (233 K)): $\delta$ 23.2 (CHC$H_3$), 24.8 (CHC$H_3$), 25.3 ($CH_2(CH_2)_2CH_2$), 25.4 (CHC$H_3$), 26.2 (CHC$H_3$), 27.9 (CHC$H_3$), 28.1 (CHC$H_3$), 39.6 ($CNCH_2CH_2NH$), 49.4 ($CH_2(CH_2)_2CH_2$), 50.2 ($CNCH_2CH_2NH$), 123.7 ($CH_{arom}$), 124.2 ($CH_{arom}$), 126.4 ($CH_{arom}$), 138.1 ($o$-$C_{arom}$), 138.8 ($o$-$C_{arom}$), 142.0 ($i$-$C_{arom}$), 143.1 ($i$-$C_{arom}$), 149.9 ($N_{pyrrolidine}$CNDipp), 157.0 (N=CNDipp), Anal. Calcd for $C_{32}H_{47}Cl_2N_5Zn{\cdot}0.7C_7H_8$: C, 63.09; H, 7.55; N, 9.97. Found: C, 63.05; H, 7.52; N, 9.89.

***VII***. A mixture of 0.50 g (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)-methyl)imidazolidinyl-2-imine and 0.20 g (2.0 mmol) of CuCl in 10 mL of tetrahydrofuran was stirred at room temperature for 16 h. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was dissolved in toluene, and the desired product **VII** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.37 g, 0.5 mmol, 53%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.10 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.77 (quint, $^3J_{HH}$ = 3.3 Hz, 4H, $CH_2(CH_2)_2CH_2$), 3.09 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C$H$CH$_3$), 3.13 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.70 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $NCH_2CH_2NH$), 3.92 (t, $^3J_{HH}$ = 8.2 Hz, 2H, $NCH_2CH_2NH$), 7.00−7.07 (m, 3H, C$H_{arom}$), 7.26 (d, $^3J_{HH}$ = 7.7 Hz, 2H, $m$-C$H_{arom}$), 7.45 (t, $^3J_{HH}$ = 7.7 Hz, 1H, $p$-C$H_{arom}$), 8.89 (br, 1H, N$H$). $^{13}$C{$^1$H} NMR (101 MHz, $CDCl_3$): $\delta$ 22.7 (CHC$H_3$), 23.6 (CHC$H_3$), 24.4 (CHC$H_3$), 24.6 (CHC$H_3$), 25.4 ($CH_2(CH_2)_2CH_2$), 28.5 (C$H$CH$_3$), 29.0 (C$H$CH$_3$), 49.0 ($CH_2(CH_2)_2CH_2$), 49.3 ($NCH_2CH_2NH$), 50.0 ($NCH_2CH_2NH$), 122.8 ($m$-C$H_{arom}$), 123.4 ($p$-C$H_{arom}$), 125.0 ($m$-C$H_{arom}$), 129.7 ($p$-C$H_{arom}$), 130.8 ($i$-$C_{arom}$), 138.7 ($o$-$C_{arom}$), 142.0 ($i$-$C_{arom}$), 145.3 ($N_{pyrrolidine}$CNDipp), 145.6 ($o$-$C_{arom}$), 161.4 (N=CNDipp). Anal. Calcd for $C_{32}H_{47}Cl_2Cu_2N_5{\cdot}0.18C_7H_8$: C, 55.63; H, 6.81; N, 9.81. Found: C, 55.59; H, 6.90; N, 9.99.

***VIII***. A mixture of 0.50 g (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)-(pyrrolidin-1-yl)methyl)imidazolidinyl-2-imine and 0.20 g (1.0 mmol) of potassium bis(trimethylsilyl)amide in 20 mL of toluene was stirred at 60 °C for 16 h. After a few minutes a precipitate could be observed. The suspension was filtered off, and the precipitate was dried in vacuo. The residue was dissolved in a toluene/diethyl ether mixture, and the desired product **VIII** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.38 g, 0.7 mmol, 71%. $^1$H NMR (400 MHz, thf-$d_8$, room temperature): $\delta$ 1.09 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.56 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.20−3.35 (br, 4H, $CH_2(CH_2)_2CH_2$), 3.23 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N$=C), 3.35 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C$H$CH$_3$), 3.62 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N$=C), 6.67−6.72 (m, 2H, $p$-C$H_{arom}$), 6.90 (d, $^3J_{HH}$ = 7.5 Hz, 2H, $m$-C$H_{arom}$), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, $m$-C$H_{arom}$). $^{13}$C{$^1$H} NMR (101 MHz, thf-$d_8$, room temperature): $\delta$ 22.7 (CHC$H_3$), 23.6 (CHC$H_3$), 24.3 (CHC$H_3$), 24.4 (CHC$H_3$), 26.0 ($CH_2(CH_2)_2CH_2$), 28.5 (C$H$CH$_3$), 48.5 ($CH_2(CH_2)_2CH_2$), 50.0 ($CNCH_2CH_2N$=C), 51.0 ($CNCH_2CH_2N$=C), 118.3 ($p$-C$H_{arom}$), 120.3 ($p$-C$H_{arom}$), 122.2 ($m$-C$H_{arom}$), 122.4 ($m$-C$H_{arom}$), 138.5 ($o$-$C_{arom}$), 143.0 ($o$-$C_{arom}$), 148.6 ($i$-$C_{arom}$), 150.8 ($N_{pyrrolidine}$CNDipp), 156.3 ($i$-$C_{arom}$), 163.7 (N=CNDipp). $^1$H NMR (400 MHz, thf-$d_8$, −50 °C (223 K)): $\delta$ 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.20 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.42 (br, 2H, $CH_2(CH_2)_2CH_2$),


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1.66 (br, 2H, $CH_2(CH_2)_2CH_2$), 2.80 (br, 2H, $CH_2(CH_2)_2CH_2$), 3.21 (br, 2H, $CH_2(CH_2)_2CH_2$), 3.33 (br, 2H, $CNCH_2CH_2N{=}C$), 3.35 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.57 (br, 2H, $CNCH_2CH_2N{=}C$), 6.71 (br, 2H, *p*-$CH_{arom}$), 6.90 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-$CH_{arom}$), 6.95 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-$CH_{arom}$). $^{13}C\{^1H\}$ NMR (101 MHz, thf-$d_8$, −50 °C (223 K)): δ 22.7 ($CHCH_3$), 23.5 ($CHCH_3$), 24.3 ($CHCH_3$), 24.5 ($CHCH_3$), 26.1 ($CH_2(CH_2)_2CH_2$), 28.5 ($CHCH_3$), 48.5 ($CH_2(CH_2)_2CH_2$), 50.0 ($CNCH_2CH_2N{=}C$), 51.0 ($CNCH_2CH_2N{=}C$), 118.3 (*p*-$CH_{arom}$), 120.2 (*p*-$CH_{arom}$), 122.2 (*m*-$CH_{arom}$), 138.2 (*o*-$C_{arom}$), 142.7 (*o*-$C_{arom}$), 148.6 (*i*-$C_{arom}$), 151.3 ($N_{pyrrolidine}CNDipp$), 156.0 (*i*-$C_{arom}$), 163.6 ($N{=}CNDipp$). Anal. Calcd for $C_{32}H_{46}KN_5$: C, 71.20; H, 8.59; N, 12.97. Found: C, 71.03; H, 8.69; N, 13.27.

***IX.*** A 1.00 g portion (2.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)-imidazolidinyl-2-imine was dissolved in 15 mL of toluene and 5 mL of tetrahydrofuran. Then a di-*n*-butylmagnesium solution (1 mL, 1 mmol, 1 M in heptane) was added at −78 °C. During stirring for 16 h the mixture was warmed room temperature. Then the mixture was heated to 50 °C and it was stirred for 1 h. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was dissolved in a toluene/pentane/tetrahydrofuran mixture, and the product **IX** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.72 g, 0.7 mmol, 66%. $^1H$ NMR (400 MHz, $C_6D_6$, room temperature): δ 1.23−1.25 (m, 48H, $CHCH_3$), 0.96−1.90 (br, 8H, $NCH_2(CH_2)_2CH_2$), 1.49 (quint, $^3J_{HH}$ = 7.4 Hz, 4 H, $O(CH_2)_2(CH_2)_2$), 2.97 (br, 16H, $CH_2(CH_2)_2CH_2$, $CHCH_3$, $CNCH_2CH_2N{=}C$), 3.50 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.89 (br, 4H, $O(CH_2)_2(CH_2)_2$), 3.97 (br, 4H, $CNCH_2CH_2N{=}C$), 7.00−7.16 (m, 12H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (101 MHz, $C_6D_6$, room temperature): δ 21.7 ($CHCH_3$), 22.8 ($CHCH_3$), 25.1 ($NCH_2(CH_2)_2CH_2$), 25.3 ($CHCH_3$), 25.4 ($O(CH_2)_2(CH_2)_2$), 26.8 ($CHCH_3$), 27.9 ($CHCH_3$), 29.0 ($CHCH_3$), 45.1 ($CNCH_2CH_2N{=}C$), 54.6 ($CNCH_2CH_2N{=}C$), 69.3 ($O(CH_2)_2(CH_2)_2$), 121.8 ($CH_{arom}$), 122.0 ($CH_{arom}$), 144.6 ($C_{arom}$), 145.4 ($C_{arom}$), 145.8 ($N_{pyrrolidine}CNDipp$), 166.6 ($N{=}CNDipp$), $^1H$ NMR (400 MHz, tol-$d_8$, room temperature): δ 1.16−1.18 (m, 48H, $CHCH_3$), 0.96−1.90 (br, 8H, $NCH_2(CH_2)_2CH_2$), 1.69 (quint, $^3J_{HH}$ = 7.4 Hz, 4 H, $O(CH_2)_2(CH_2)_2$), 2.94 (br, 16H, $CH_2(CH_2)_2CH_2$, $CHCH_3$, $CNCH_2CH_2N{=}C$), 3.43 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.87 (br, 4H, $O(CH_2)_2(CH_2)_2$), 3.92 (br, 4H, $CNCH_2CH_2N{=}C$), 6.90−7.06 (m, 12H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (101 MHz, tol-$d_8$, room temperature): δ 21.7 ($CHCH_3$), 22.8 ($CHCH_3$), 25.1 ($NCH_2(CH_2)_2CH_2$), 25.3 ($CHCH_3$), 25.5 ($O(CH_2)_2(CH_2)_2$), 26.8 ($CHCH_3$), 27.9 ($CHCH_3$), 29.0 ($CHCH_3$), 45.1 ($CNCH_2CH_2N{=}C$), 54.6 ($CNCH_2CH_2N{=}C$), 69.3 ($O(CH_2)_2(CH_2)_2$), 121.9 ($CH_{arom}$), 122.0 ($CH_{arom}$), 144.6 ($C_{arom}$), 145.4 ($C_{arom}$), 145.8 ($N_{pyrrolidine}CNDipp$), 166.7 ($N{=}CNDipp$), $^1H$ NMR (400 MHz, tol-$d_8$, −50 °C): δ 0.89 (br, 2H, $CH_2(CH_2)_2CH_2$), 0.98−1.47 (m, 52H, $CHCH_3$, $NCH_2(CH_2)_2CH_2$), $OCH_2(CH_2)_2CH_2$),), 1.55 (br, 2H, $NCH_2(CH_2)_2CH_2$), 1.96 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$,), 2.25−2.32 (m, 2H, $NCH_2(CH_2)_2CH_2$), 2.56 (t, $^3J_{HH}$ = 9.4 Hz, 2H, $CNCH_2CH_2N{=}C$), 2.81−3.00 (m, 6H, $CHCH_3$, $CNCH_2CH_2N{=}C$, $NCH_2(CH_2)_2CH_2$), 3.35−3.43 (m, 8H, $CHCH_3$, $NCH_2(CH_2)_2CH_2$), 3.65−3.72 (m, 2H, $OCH_2(CH_2)_2CH_2$), 3.78−3.84 (m, 4H, $CNCH_2CH_2N{=}C$, $OCH_2(CH_2)_2CH_2$), 4.04−4.10 (m, 2H, $CNCH_2CH_2N{=}C$), 6.94−7.21 (m, 12H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (101 MHz, tol-$d_8$, −50 °C): δ 21.2 ($CHCH_3$), 21.5 ($CHCH_3$), 22.7 ($CHCH_3$), 22.9 ($CHCH_3$), 25.0 ($CH_2(CH_2)_2CH_2$), 25.2 ($CHCH_3$), 25.3 ($CH_2(CH_2)_2CH_2$), 25.4 ($CH_2(CH_2)_2CH_2$), 25.6 ($CHCH_3$), 26.1 ($CHCH_3$), 27.5 ($CHCH_3$), 27.7 ($CHCH_3$), 28.2 ($CHCH_3$), 28.9 ($CHCH_3$), 29.3 ($CHCH_3$), 44.5 ($CNCH_2CH_2N{=}C$), 45.5 ($NCH_2(CH_2)_2CH_2$), 47.8 ($NCH_2(CH_2)_2CH_2$), 54.6 ($CNCH_2CH_2N{=}C$), 68.9 ($O(CH_2)_2(CH_2)_2$), 120.8 (*m*-$CH_{arom}$), 121.5 (*m*-$CH_{arom}$), 121.9 (*m*-$CH_{arom}$), 122.3 (*m*-$CH_{arom}$), 123.8 (*p*-$CH_{arom}$), 124.3 (*p*-$CH_{arom}$), 137.2 (*o*-$C_{arom}$), 139.3 (*o*-$C_{arom}$), 139.8 (*o*-$C_{arom}$), 142.3 (*o*-$C_{arom}$), 144.4 (*i*-$C_{arom}$), 145.1 (*i*-$C_{arom}$), 145.9 ($N_{pyrrolidine}CNDipp$), 166.2 (N = $CNDipp$), $^1H$ NMR (400 MHz, tol-$d_8$, 70 °C): δ 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHCH_3$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHCH_3$), 1.18 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHCH_3$), 1.25 (br, 8H, $NCH_2(CH_2)_2CH_2$), 1.49 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHCH_3$), 1.58 (quin, $^3J_{HH}$ = 3.2 Hz, 4H, $O(CH_2)_2(CH_2)_2$), 2.66 (br, 8H, $NCH_2(CH_2)_2CH_2$), 2.93 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.02 (t, $^3J_{HH}$ = 7.5 Hz, $CNCH_2CH_2N{=}C$), 3.44 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHCH_3$), 3.89 (br, 4H, $O(CH_2)_2(CH_2)_2$), 3.92 (t, $^3J_{HH}$ = 7.5 Hz, 4H, $CNCH_2CH_2N{=}C$), 6.85−7.06 (m, 12H, $CH_{arom}$), $^{13}C\{^1H\}$ NMR (101 MHz, tol-$d_8$, 70 °C): δ 21.9 ($CHCH_3$), 22.7 ($CHCH_3$), 25.1 ($CH_2(CH_2)_2CH_2$), 25.1 ($CHCH_3$), 25.6 ($O(CH_2)_2(CH_2)_2$), 26.6 ($CHCH_3$), 28.0 ($CHCH_3$), 29.0 ($CHCH_3$), 45.4 ($CNCH_2CH_2N{=}C$), 47.1 ($CH_2(CH_2)_2CH_2$), 54.7 ($CNCH_2CH_2N{=}C$), 69.3 ($O(CH_2)_2(CH_2)_2$), 122.1 (*m*-$CH_{arom}$), 122.1 (*p*-$CH_{arom}$), 122.8 ($CH_{arom}$), 138.5 (*o*-$C_{arom}$), 142.0 (*o*-$C_{arom}$), 144.7 (*i*-$C_{arom}$), 145.5 (*i*-$C_{arom}$), 145.8 ($N_{pyrrolidine}CNDipp$), 167.1 ($N{=}NDipp$). Anal. Calcd for $C_{68}H_{100}MgN_{10}O{\cdot}0.5C_4H_8O$: C, 74.14; H, 9.24; N, 12.38. Found: C, 73.78; H, 9.18; N, 12.72.

***X.*** A mixture of 0.50 g (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)-methyl)imidazolidinyl-2-imine and 0.09 g (1.0 mmol) of $AlH_3{\cdot}NMe_3$ in 8 mL of tetrahydrofuran was stirred at room temperature for 16 h. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was dissolved in toluene, and the desired product **X** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.27 g, 0.5 mmol, 51%. $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.27 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.70 (quin, $^3J_{HH}$ = 3.2 Hz, 4H, $CH_2(CH_2)_2CH_2$), 3.02 (quin, $^3J_{HH}$ = 3.2 Hz, 4H, $CH_2(CH_2)_2CH_2$), 3.33 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHCH_3$), 3.41 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHCH_3$), 3.56 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N{=}C$), 3.72 (br, 2H, $AlH_2$), 3.97 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N{=}C$), 7.12−7.27 (m, 6H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 23.5 ($CHCH_3$), 24.7 ($CHCH_3$), 25.5 ($CH_2(CH_2)_2CH_2$), 26.7 ($CHCH_3$), 28.3 ($CHCH_3$), 28.5 ($CHCH_3$), 49.2 ($CNCH_2CH_2N{=}C$), 50.2 ($CH_2(CH_2)_2CH_2$), 51.1 ($CNCH_2CH_2N{=}C$), 123.9 (*m*-$CH_{arom}$), 124.7 (*m*-$CH_{arom}$), 126.1 (*p*-$CH_{arom}$), 127.4 (*p*-$CH_{arom}$), 137.9 (*i*-$C_{arom}$), 139.0 (*i*-$C_{arom}$), 144.2 (*o*-$C_{arom}$), 145.6 (*o*-$C_{arom}$), 155.1 ($N_{pyrrolidine}CNDipp$), 156.9 ($N{=}CNDipp$); $^{27}Al$ NMR (104 MHz, $CDCl_3$): δ no signal. IR ($cm^{-1}$): ν($CH_3$) 2962, ν($AlH_2$) 1833 and 1802, ν(CN) 1628. Anal. Calcd for $C_{32}H_{48}N_5Al$: C, 72.55; H, 9.13; N, 13.22. Found: C, 72.79, H, 9.10, N, 13.26.

***XI.*** A 0.50 g portion (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)-imidazolidinyl-2-imine was dissolved in 20 mL of toluene. The solution was heated to 90 °C. At this temperature a trimethylaluminum solution (0.5 mL, 1.0 mmol, 2 M in toluene) was added dropwise. The mixture was stirred at 90 °C for 16 h. Then the reaction mixture was warmed to room temperature. After that the mixture was filtered off and the filtrate was concentrated in vacuo. The residue was dissolved in a toluene/pentane mixture, and the product **XI** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.40 g, 0.7 mmol, 71%. $^1H$ NMR (400 MHz, $CDCl_3$): δ −0.93 (s, 6H, $Al(CH_3)_2$), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.21 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.24 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.25 (d, $^3J_{HH}$ = 6.8 Hz, 6H, $CHCH_3$), 1.73 (quin, $^3J_{HH}$ = 3.4 Hz, 4H, $CH_2(CH_2)_2CH_2$), 2.99 (quin, $^3J_{HH}$ = 3.4 Hz, 4H, $CH_2(CH_2)_2CH_2$), 3.31 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHCH_3$), 3.34 (sept, $^3J_{HH}$ = 6.8 Hz, 2H, $CHCH_3$), 3.48 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N{=}C$), 3.87 (t, $^3J_{HH}$ = 7.1 Hz, 2H, $CNCH_2CH_2N{=}C$), 7.09−7.25 (m, 6H, $CH_{arom}$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDl_3$): δ −10.0 ($Al(CH_3)_2$), 23.7 ($CHCH_3$), 24.3 ($CHCH_3$), 25.1 ($CHCH_3$), 25.4 ($CH_2(CH_2)_2CH_2$), 26.3 ($CHCH_3$), 28.0 ($CHCH_3$), 28.8 ($CHCH_3$), 49.2 ($CNCH_2CH_2N{=}C$), 49.9 ($CH_2(CH_2)_2CH_2$), 51.1 ($CNCH_2CH_2N{=}C$), 123.6 (*m*-$CH_{arom}$), 124.4 (*m*-$CH_{arom}$), 125.0 (*p*-$CH_{arom}$), 127.1 (*p*-$CH_{arom}$), 137.9 (*i*-$C_{arom}$), 141.4 (*i*-$C_{arom}$), 144.1 (*o*-$C_{arom}$), 144.7 (*o*-$C_{arom}$), 153.3 ($N_{pyrrolidine}CNDipp$), 158.5 ($N{=}CNDipp$), $^{27}Al$ NMR (104 MHz, $CDCl_3$): δ no signal. Anal. Calcd for $C_{34}H_{52}N_5Al$: C, 73.21; H, 9.40; N, 12.56. Found: C, 73.21, H, 9.44, N, 12.51.

***XII.*** A 0.50 g portion (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)-


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imidazolidinyl-2-imine was dissolved in 20 mL of toluene. Then a trimethylaluminum solution (1 mL, 2 mmol, 2 M in toluene) was added at room temperature. The mixture was stirred for 16 h. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was dissolved in toluene, and the product **XII** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.34 g, 0.5 mmol, 54%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ −1.36 (s, 9H, Al($CH_3$)$_3$), −0.93 (br, 6H, Al($CH_3$)$_2$), 1.10 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.22 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.27 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.32 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.80 (br, 4H, CH$_2$(C$H_2$)$_2$C$H_2$), 3.02 (br, 8H, C$H$CH$_3$,C$H_2$(CH$_2$)$_2$C$H_2$), 3.69 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNC$H_2$CH$_2$N=C) 3.83 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNCH$_2$C$H_2$N=C), 7.15 (m, 5H, C$H_{arom}$), 7.26 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, $p$-C$H_{arom}$). $^{13}$C{$^{1}$H} NMR (101 MHz, $CDl_3$): $\delta$ −10.2 (Al($CH_3$)$_2$), −6.1 (Al($CH_3$)$_3$), 23.5 (CH$CH_3$), 23.6 (CH$CH_3$), 24.7 (CH$CH_3$), 25.5 (CH$_2$(CH$_2$)$_2$CH$_2$), 25.8 (CH$CH_3$), 28.2 (C$HCH_3$), 30.0 (C$HCH_3$), 49.1 (CNCH$_2$CH$_2$N=C), 49.4 (CNCH$_2$CH$_2$N=C), 50.2 (C$H_2$(CH$_2$)$_2$C$H_2$), 124.7 ($m$-C$H_{arom}$), 125.1 ($m$-C$H_{arom}$), 126.0 ($p$-C$H_{arom}$), 128.0 ($p$-C$H_{arom}$), 136.5 ($i$-C$_{arom}$), 139.2 ($i$-C$_{arom}$), 142.9 ($o$-C$_{arom}$), 143.6 ($o$-C$_{arom}$), 152.4 (N$_{pyrrolidine}$CNDipp), 160.9 (N=CNDipp). $^{27}$Al NMR (104 MHz, $CDCl_3$): $\delta$ no signal. Anal. Calcd for $C_{37}H_{61}AlN_5$: C, 70.55; H, 9.76; N, 11.12. Found: C, 70.84, H, 9.81, N, 11.28.

***XIII***. A 0.50 g portion (1.0 mmol) of (*E*)-*N*-(2,6-diisopropylphenyl)-1-((*E*)-((2,6-diisopropylphenyl)imino)(pyrrolidin-1-yl)methyl)-imidazolidinyl-2-imine was dissolved in 20 mL of toluene. Then a diethylzinc solution (1.2 mL, 1.2 mmol, 1 M in hexane) was added at −78 °C. During stirring for 16 h the mixture was warmed to room temperature. The mixture was filtered off, and the filtrate was concentrated in vacuo. The residue was taken up in pentane. The product **XIII** was crystallized in the form of colorless blocks at room temperature. Colorless crystals, 0.31 g, 0.3 mmol, 52%. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ −0.08 (quart, $^{3}J_{HH}$ = 8.1 Hz, 2H, ZnC$H_2$CH$_3$), 0.13 (quart, $^{3}J_{HH}$ = 8.1 Hz, 2H, ZnC$H_2$CH$_3$), 0.82 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, ZnCH$_2$C$H_3$),), 0.98 (quint, $^{3}J_{HH}$ = 3.3 Hz, 4H, CH$_2$(C$H_2$)$_2$CH$_2$), 1.09 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, ZnCH$_2$C$H_3$), 1.12 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.19 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.35−1.40 (m, 4H, CH$_2$(C$H_2$)$_2$CH$_2$), 1.27 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.29 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.39 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.42 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.43 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 1.29 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, CHC$H_3$), 2.55 (quint, $^{3}J_{HH}$ = 3.3 Hz, 4H, C$H_2$(CH$_2$)$_2$C$H_2$), 3.07 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNC$H_2$CH$_2$N=C), 3.21 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C$H$CH$_3$), 3.31 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNC$H_2$CH$_2$N=C), 3.45 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C$H$CH$_3$), 3.48−3.54 (m, 4H, C$H_2$(CH$_2$)$_2$C$H_2$), 3.51 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNCH$_2$C$H_2$N=C), 3.53 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C$H$CH$_3$), 3.74 (sept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C$H$CH$_3$), 3.90 (t, $^{3}J_{HH}$ = 7.1 Hz, 2H, CNCH$_2$C$H_2$N=C), 7.00−7.28 (m, 12H, C$H_{arom}$). $^{13}$C{$^{1}$H} NMR (101 MHz, $CDCl_3$): $\delta$ −1.5 (ZnCH$_2$CH$_3$), −0.3 (ZnCH$_2$CH$_3$), 11.6 (ZnCH$_2$CH$_3$), 12.3 (ZnCH$_2$CH$_3$), 22.8 (CH$CH_3$), 23.1 (CH$CH_3$), 23.7 (CH$CH_3$), 24.2 (CH$CH_3$), 24.4 (CH$CH_3$), 24.6 (CH$CH_3$), 24.9 (CH$CH_3$), 25.1 (CH$CH_3$), 25.3 (CH$_2$(CH$_2$)$_2$CH$_2$), 25.6 (CH$_2$(CH$_2$)$_2$CH$_2$), 28.5 (CH$CH_3$), 28.5 (CH$CH_3$), 28.8 (CH$CH_3$), 29.0 (C$HCH_3$), 45.3 (CNCH$_2$CH$_2$N=C), 48.4 (CH$_2$(CH$_2$)$_2$CH$_2$), 49.0 (CNCH$_2$CH$_2$N=C), 49.2 (CH$_2$(CH$_2$)$_2$CH$_2$), 50.3 (CNCH$_2$CH$_2$N=C), 51.4 (CNCH$_2$CH$_2$N=C), 121.9 ($m$-C$H_{arom}$), 122.8 ($m$-C$H_{arom}$), 123.5 ($m$-C$H_{arom}$), 124.2 ($m$-C$H_{arom}$), 125.0 ($p$-C$H_{arom}$), 126.1 ($p$-C$H_{arom}$), 126.7 ($p$-C$H_{arom}$), 126.8 ($p$-C$H_{arom}$), 138.5 ($o$-C$_{arom}$), 140.8 ($o$-C$_{arom}$), 141.5 ($o$-C$_{arom}$), 142.0 ($i$-C$_{arom}$), 143.9 ($o$-C$_{arom}$), 145.0 ($i$-C$_{arom}$), 146.5 ($i$-C$_{arom}$), 146.7 (N$_{pyrrolidine}$CNDipp), 149.4 ($i$-C$_{arom}$), 154.9 (N$_{pyrrolidine}$CNDipp), 158.6 (N=CNDipp), 162.1 (N = CNDipp); Anal. Calcd for $C_{68}H_{102}N_{10}Zn_2$: C, 68.61; H, 8.64; N, 11.77. Found: C, 68.34, H, 8.59, N, 11.62.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03093.

Additional figures, experimental and computational details, crystallographic data, NMR and IR spectra, and XYZ coordinates (PDF)

### Accession Codes

CCDC 1539253, 1812648, and 1954639−1954648 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.


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## ■ ABBREVIATIONS

Dipp, 2,6-diisopropylphenyl; DMP, 2,6-dimethylphenyl; Nac-Nac, $\beta$-diiminate

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