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The Flexible Coordination Modes of Guanidine Ligands in Zn Alkyl and Halide Complexes: Chances for Catalysis

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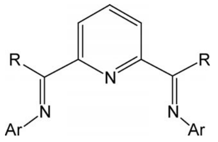
Due to their high basicity, guanidines are versatile ligand systems. In principal, they could use both their imino and amino nitrogen to establish a dative metal–N bond. However, generally only the imino N of a guanidine ligand is bound to a metal. Herein we present some examples in which both the imino and amino groups of guanidine ligands are directly engaged in the bonding to a metal ion. Under certain conditions the amino group could establish an additional link to a metal center acting as a hemilabile ligand. This result is likely to be of relevance for catalytic reactions, demonstrating the possibility to stabilize a vacancy at the metal (for instance generated by ligand dissociation).

Introduction

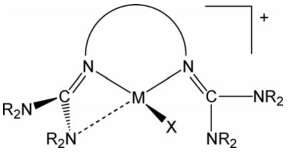
Guanidines and guanidinates are now well established as versatile ligand systems.[1,2] For example, guanidine-stabilized zinc complexes were shown to be promising catalysts for the synthesis of polylactide.[3] The ring-opening polymerization of lactide could also be accomplished with zinc guanidinate complexes.[4] With Cu^I guanidine complexes enzymatic reactivity can be modelled. Recently, a Cu^I complex of a tripodal, superbasic and sterically encumbered tris(tetramethylguandino)tren (TMG3tren) ligand, which forms the first 1:1 Cu/O_2 complex featuring an end-on-coordinated superoxo (O_2^-) unit and its chemistry were reported.[5,6] Other Cu and also Fe complexes of chelating guanidines were synthesized by Henkel, Tamm et al.[7,8] Group 10 (Ni, Pd and Pt) and Zn, Mg and Al complexes of chelating guanidines and their application in some catalytic reactions were studied by our group.[9]

Bis(imines) are known to be excellent ligands in late-transition metal complexes that can be applied as catalysts in olefin polymerization. Especially sterically demanding bis(arylimino)pyridine ligands, 2,6-$(ArN{=}CR)_2C_5H_3N$, have been studied intensively in the past (see Scheme 1).[10] The properties of the Ar substituents (their steric requirements) generally control the molecular weight of the oligomers or polymeric chains. The two amino groups attached to the imino C atom in guanidines increase the basicity and change the electronic properties. However, they generally are not directly involved in the bonding to the metal.



Scheme 1.

In principal, the amino group could act as a hemilabile ligand. Hence it should be possible to stabilize a vacancy at the metal cation formed by ligand dissociation by an interaction of the metal with one of the amino groups, leading to a situation as sketched in Scheme 2 for the example of a bis(guanidine) ligand and a four-coordinate metal ion (a planar coordination might be better suited than the shown tetrahedral one).



Scheme 2.

However, up to date no evidence was found for such a direct engagement of the amino group in the bonding to a metal.[2] On the other hand, in some reactions of guanidines involving inorganic Lewis acids, coordination of the Lewis acid at the amino group is believed to be the first step in decomposition pathways. One such example is provided by thermal decomposition of the tetramethylguanidine–borane adduct sketched in Equation (1).[11] The BH_3 group migrates to one of the amino N atoms. Then a 1,4-dehydrogenation reaction follows leading to decomposition to give finally $(HBNMe)_n$ oligomers. The Ga analogue $H_3Ga\cdot N(H)C(NMe_2)_2$ was also observed to decompose upon mild

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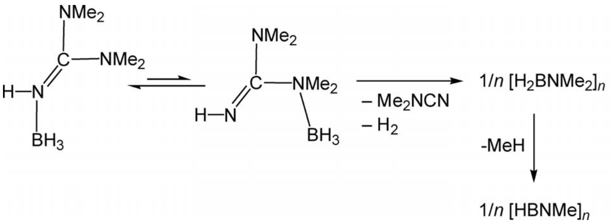
heating to give, besides other products, the oligonuclear compound $HN\{[HGaNMe][H_2GaNC(NMe_2)_2]\}_3GaH$.[12] The [HGaNMe] groups within this species are presumably the products of similar processes.



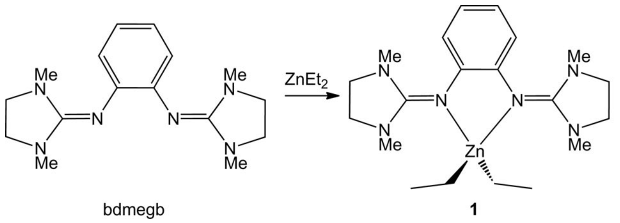
(1)

Thus removal of guanidine amino groups in the presence of inorganic Lewis acids is not unprecedented. Decomposition leading also to elimination of an amino group was also reported by Barry et al. for guanidinate complexes,[13] where thermal decomposition of copper guanidinates was shown to lead to carbodiimides.

In a previous work we analysed the structure and fluxional behaviour in solution of several Zn dialkyl and Zn dihalide complexes of bis(guanidines).[14] In all studied complexes, only the imine N atoms coordinated to the metal. Herein, we will show now that Zn complexes can indeed be designed in which both the imino and an amino group of the guanidine ligands are directly involved in the metal–ligand bonding. The bonding situation will be shown to be different to that in Scheme 2.

Results and Discussion

In this section we discuss several Zn dialkyl and also chloride complexes which should highlight the role of the amino groups within the guanidine ligands. In the first set of experiments, we used the bis(guanidine) ligand bdmegb [1,2-bis(*N*,*N'*-dimethyl-*N*,*N'*-ethyleneguanidino)benzene], see Equation (2), which we already introduced as a ligand previously.[15] The complex $[(bdmegb)ZnEt_2]$ (**1**) can be synthesized directly from bdmegb and $ZnEt_2$ at room temperature in more than 70% yield [see Equation (2)]. In the ^1H NMR spectrum, the two ethyl groups show at –0.33 (CH_2) and 0.99 (CH_3). The molecular structure as determined from X-ray diffraction is visualized in Figure 1. The two imino N atoms of the guanidino groups form coordinative bonds to the metal ion [with Zn–N bond lengths of 222.88(18) and 220.57(15) pm]. The C=N double bond lengths slightly increase (to ca. 131 pm) with respect to the values in the uncoordinated bdmegb (ca. 128 pm).[15] The C–Zn–C bond angle amounts to 136.08(8)°. The amino groups do not participate directly in the coordinative bonding. The complex is thermally robust and shows no sign of decomposition via alkylation of the guanidino C=N double bond. Unfortunately, attempts to synthesize cationic alkyl complexes of Zn with this or other guanidine ligands by protonation of an alkyl group failed so far.



(2)

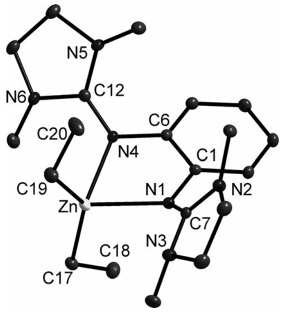


Figure 1. Molecular structure of **1** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree): Zn–N1 222.88(18), Zn–N4 220.57(15), Zn–C17 201.22(19), Zn–C19 201.5(2), N1–C1 141.3(2), N1–C7 130.7(2), N2–C7 136.0(2), N3–C7 138.0(2), N4–C6 141.4(2), N4–C12 130.6(2), N5–C12 136.8(2), N6–C12 136.9(2), N1–Zn–N4 76.08(5), C17–Zn–C19 136.08(8), C1–N1–C7 121.21(16), C6–N4–C12 121.64(15), N2–C7–N3 108.66(16), N5–C12–N6 109.16(15).

A very different bonding situation, already in a neutral complex, can be realized with the guanidine 2-(*N*,*N'*-diisopropylguanidino)pyridine [diprgpy, see Equation (3)] featuring reactive N–H bonds. In addition to the guanidino function, this ligand offers the pyridine N atom for metal coordination. It was prepared according to a literature procedure[16] (for analytical data, see ref.[17]) and subsequently brought to reaction with $ZnMe_2$. The analysis of the product showed that only one of the N–H groups reacts. Hence a signal at δ = 3.42 ppm in the ^1H NMR spectrum can be assigned to the remaining N–H proton. The NMR spectra also reveal the presence of methyl groups directly attached to Zn^{II}, giving rise to a signal at δ = 0.00 ppm in the ^1H NMR spectrum. A crystal structure analysis finally showed the product to be the new dinuclear Zn complex $[(C_6H_4N)NC(N(H)i\mathrm{Pr})(Ni\mathrm{Pr})ZnMe]_2$ (**2**). Its molecular structure is visualized in Figure 2. Dimerization allows each Zn^{II} to be tetra-coordinated. The molecule contains two folded six-membered rings, each with three N, two C and one Zn atom, which are linked together through two Zn–N bonds. The structural data indicate the formation of a strong bond between the N atom of the deprotonated amino group and Zn [Zn–N3 202.38(15 pm)]. The former C=N double bond (N2–C6) of the guanidine is elongated considerably [to as much as 137.03(19) pm], being now similar in length to the C6–N4 single bond [137.3(2) pm]. At the same time, the N3–C6 bond shrinks to 131.68(19) pm. Thus the NC double bond within the guanidino group shifts as indicated in the sketched Lewis structure of **2** in Equation (3). Also noteworthy is the short Zn–N1 bond length of 206.80(15) pm, being much shorter than Zn–N2′ [214.09(12) pm]. According to our analytical data, the dimeric assembly is stable in solution. It should be emphasized that the bonding mode of the guanidinate [2-NC(N(H)*i*Pr)(N*i*Pr)]-(C_6H_4N) is very different to that generally found in acyclic Zn guanidinates (allyl-type form and κ^2 bonding mode[4] or bridging mode in the case of $NC(NMe_2)_2$ [18]) or bicyclic Zn guanidinates (bridging coordination of various forms).[19]

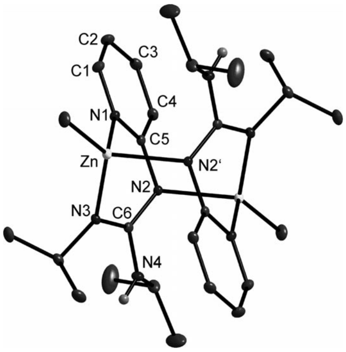
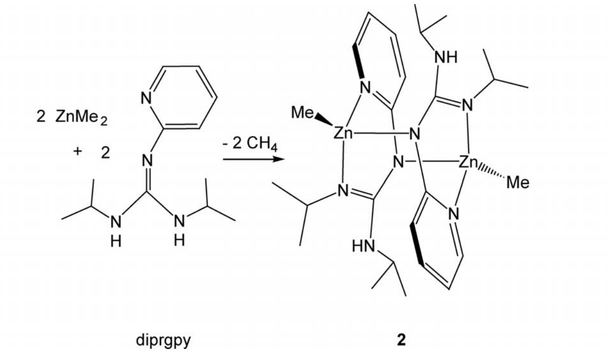
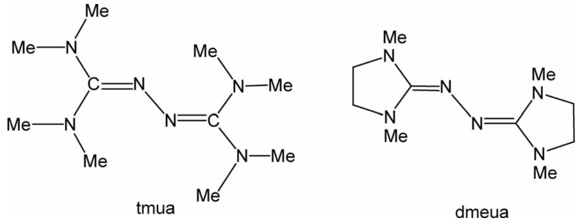


Figure 2. Molecular structure of **2** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree): Zn–N1 206.80(15), Zn–N2′ 214.09(12), Zn–N3 202.38(15), Zn–C13 198.67(17), N1–C1 135.26(19), N2–C5 138.05(18), N2–C6 137.03(19), N3–C6 131.68(19), N4–C6 137.3(2), C1–C2 137.2(2), C2–C3 139.5(2), C3–C4 137.5(2), C4–C5 140.9(2), N1–Zn–N2′ 93.71(6), N1–Zn–N3 87.29(6), N2′–Zn–N3 98.06(5), Zn1–N1–C5 116.95(9), C5–N2–C6 121.39(12), Zn1–N3–C6 115.86(10), N3–C6–N4 122.32(13).



(3)

To obtain a situation in which a guanidino NR_2 group ($R \neq H$) interacts with Zn^{II}, the ligand system has to be further modified. For this purpose, we prepared the two new bis(guanidines) tetramethylurea azine (tmua) and *N*,*N*′-dimethylethyleneurea azine (dmeua, see Scheme 3) starting from hydrazine. The molecular structures as derived for tmua and dmeua are illustrated in Figure 3. The structures can be compared directly with that of the urea azine $[Cy(H)N]_2C=N–N=C[N(H)Cy]_2$ (Cy = cyclohexyl), which was recently presented by Villiers, Thuéry and Ephritikhine [20] and used for the synthesis of uranium complexes. The N–N bonds in tmua and dmeua (N1–N1′) measure 141.5(2) and 141.60(13) pm, respectively, and are thus slightly shorter than that in $[Cy(H)N]_2C=N–N=C[N(H)Cy]_2$ [142.90(18) pm]. With 130.58(17) pm in tmua and 129.55(9) pm in dmeua, the C=N imino bond lengths (N1–C1) fall in a characteristic region for guanidines {the corresponding bond in $[Cy(H)N]_2C=N–N=C[N(H)Cy]_2$ measures 129.71(15) pm}.



Scheme 3.

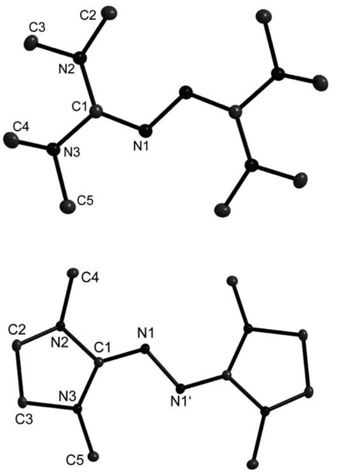


Figure 3. Molecular structures of tmua and dmeua as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters for tmua (distances in pm, angles in degree): N1–N1′ 141.5(2), N1–C1 130.58(17), N2–C1 137.12(16), N3–C1 140.27(17), N1′–N1–C1 113.24(13), N2–C1–N3 114.56(11). Selected structural parameters for dmeua (distances in pm, angles in degree): N1–N1′ 141.60(13), N1–C1 129.55(9), N2–C1 139.41(10), N3–C1 139.76(10), N1′–N1–C1 114.17(8), N2–C1–N3 108.36(6).

The two ligands are thermally stable and can be purified by sublimation at 90 °C without decomposition.

Both ligands were brought to reaction with $ZnEt_2$ and $ZnCl_2$. The products of these reactions turned out to be extremely water and moisture sensitive. Hence for reactions with $ZnCl_2$ in THF, Et_2O or toluene solutions, precipitation of small amounts of crystalline product suitable for X-ray diffraction was observed if the reaction mixture is brought into contact with air. Figure 4 displays the structures derived from this analysis. They consist of $[(tmuaH)ZnCl_3]$, **3**, and $[(dmeuaH)ZnCl_3]$, **4**, molecular units. In both cases, the Zn^{II} ion is coordinated only to one of the imino N atoms of the urea azines. In the case of **4**, an intramolecular N–H···Cl bond is established (see Figure 4, b). Complex **3** prefers instead formation of intermolecular N–H···Cl bonds (see Figure 4, a), in addition to C–H···Cl contacts. The Zn–N bond lengths measure 203.1(2) pm in **3** and 206.7(3) pm in **4**.

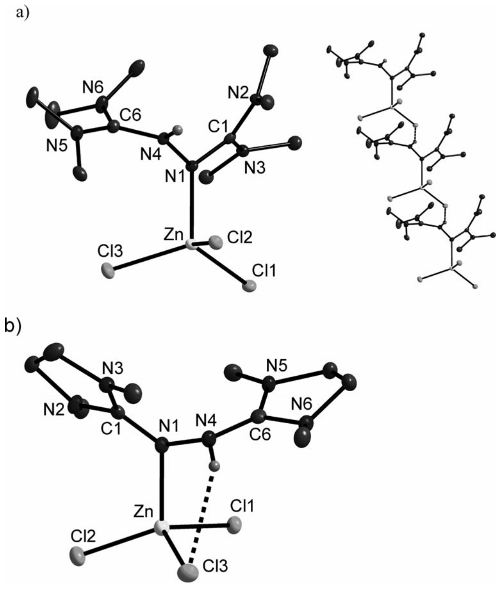


Figure 4. a) Molecular structure of **3** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree): Zn–N1 203.1(2), Zn···N4 288.1(4), Zn–Cl1 224.08(9), Zn–Cl2 229.01(9), Zn–Cl3 226.55(9), N1–N4 143.6(3), N1–C1 134.4(3), N2–C1 135.3(3), N3–C1 134.6(3), N4–C6 135.3(3), N5–C6 133.5(4), N6–C6 133.7(4), Zn–N1–N4 111.22(16), Cl1–Zn–N1 111.54(7), Cl2–Zn–N1 98.24(7), Cl3–Zn–N1 106.47(7), C1–N1–N4 114.8(2), N1–N4–C6 117.0(2), N2–C1–N3 118.6(2), N5–C6–N6 120.6(3); b) Molecular structure of **4** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree): Zn–N1 206.7(3), Zn···N4 286.2(4), Zn–Cl1 224.62(14), Zn–Cl2 223.70(12), Zn–Cl3 229.67(13), N1–N4 142.3(5), N1–C1 133.4(5), N2–C1 135.5(5), N3–C1 133.6(5), N4–C6 134.0(5), N5–C6 132.2(5), N6–C6 135.6(5), Zn–N1–N4 108.8(2), Cl1–Zn–N1 102.23(11), Cl2–Zn–N1 114.48(10), Cl3–Zn–N1 97.39(10), C1–N1–N4 112.4(3), N1–N4–C6 121.0(4), N2–C1–N3 111.1(4), N5–C6–N6 111.8(4).

A small amount of crystalline product was isolated from reaction between tmua and $ZnEt_2$. The NMR spectra showed the preservation of the ethyl groups attached to Zn. Hence signals at –0.24 ppm (quartet) and 1.12 ppm (triplet) in the ^1H NMR spectrum can be assigned to the ethyl groups. These chemical shifts compare with values of –0.33 ppm (quartet) and 0.99 ppm (triplet) measured in **1**. The NMR spectra also indicate the coordination of one tmua ligand. Unfortunately, due to the extremely high moisture sensitivity, no yield or elemental analysis can be provided. However, a crystal structure analysis of the crystalline product proved possible. In agreement with the NMR spectroscopic data, this analysis showed the product to be the complex [(tmua)$ZnEt_2$], **5**. Its molecular structure is displayed in Figure 5 (a). Importantly, the Zn^{II} is bonded not only to an imino N atom, but also to an amino N atom. With 214.3(2) pm, the Zn–N1(imino) bond is shorter than the two Zn–N(imino) bonds in **1**. The Zn–N6(amino) bond length measures 236.3(2) pm. Although it is significantly longer than Zn–N1, the value clearly indicates a bonding situation between the amino N6 atom and Zn^{II}. Hence this complex is a rare example for the direct involvement of an amino group in the coordinative bonding, while the imino group of the same guanidino unit is not coordinated. With 71.64(8)°, the N1–Zn–N6 bond angle is slightly smaller than in **1** [76.08(5)°], while the two Zn–C bond lengths [201.0(3) and 201.2(3) pm] are similar to those in **1**.

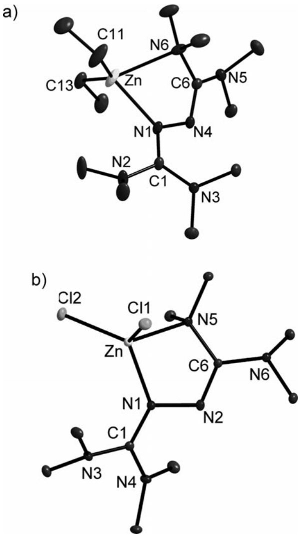
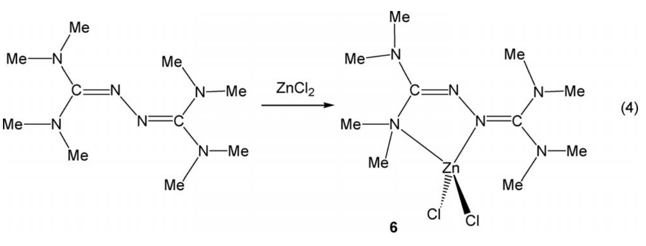


Figure 5. a) Molecular structure of **5** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree):Zn–N1 214.3(2), Zn–N6 236.3(2), Zn–C11 201.0(3), Zn–C13 201.2(3), N1–N4 141.4(3), N1–C1 130.4(3), N2–C1 136.9(3), N3–C1 136.5(3), N4–C6 128.6(3), N5–C6 139.3(3), N6–C6 142.3(3), N1–Zn–N6 71.64(8), C11–Zn–C13 133.24(13), C1–N1–N4 114.8(2), C6–N4–N1 114.1(2), N2–C1–N3 115.1(2), N5–C6–N6 118.0(2); b) Molecular structure of **6** as derived from X-ray diffraction. Ellipsoids are drawn at the 50% probability level. Selected structural parameters (distances in pm, angles in degree): Zn–Cl1 221.89(8), Zn–Cl2 221.06(7), Zn–N1 200.08(19), Zn–N5 215.5(2), N1–C1 132.1(3), N2–C6 129.0(3), N5–C6 144.9(3), N6–C6 138.0(3), N3–C1 136.8(3), N4–C1 135.5(3), N1–N2 141.4(2), Cl1–Zn–Cl2 118.10(3), N1–Zn–N5 78.69(8), C1–N1–N2 115.11(18), N1–N2–C6 114.31(18).

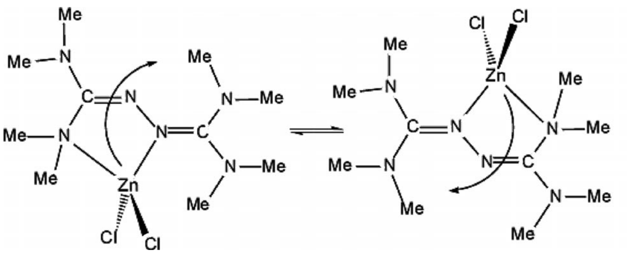
The corresponding dichloride complex [(tmua)$ZnCl_2$] (**6**) turned out to be more stable [see Equation (4)], and consequently we were able to study it in more detail. Its molecular structure is depicted in Figure 5 (b).



(4)

Like in the ethyl complex, Zn^{II} is coordinated by one imino N and one amino N atom. With 200.08(2) pm, the Zn–N1 bond length is shorter than the Zn–N5 bond length [215.5(2) pm]. As anticipated, these distances indicate that guanidine-Zn bonding is stronger in **6** than in **5**. Interestingly, the N5–C6 bond length is elongated [144.9(3) pm], and at the same time the N2–C6 bond length shortened [129.0(3) pm]. In this respect **6** can be regarded as a model for an intermediate on the way to cleavage of the N5–C6 bond. The bonding mode in **6** can be compared with that found in some complexes of guanidino-substituted phosphanes, in which an amino group N atom and a P atom are coordinated to a metal.[21] We calculated the structure of complex **6** using the B3LYP functional in combination with the def2-TZVP basis set. A comparison between calculated and experimentally determined structures can be found in Table S1 of the Supporting Information. Generally, the calculated gas-phase structure is in agreement with the experimentally derived one. However, relatively large deviations were encountered for the Zn–N bond lengths [exp. values of 200.16(19) and 215.52(20) pm for Zn–N1 and Zn–N5 vs. calculated ones of 207.32 and 232.18 pm, respectively]. Unfortunately, It was so far impossible to isolate a complex in which a second Zn^{II} ion coordinates to the tmua ligand.

Information about the molecule in solution was derived from NMR spectroscopic measurements. We first synthesized the ^{15}N-enriched ligand [(Me$_2$N)$_2$C^{15}N]$_2$ (^{15}N$_2$-tmua) to obtain better ^{15}N NMR spectra. Figure 6 shows a ^{15}N–^{1}H correlation for [(^{15}N$_2$-tmua)ZnCl$_2$]. VT NMR spectra in the region of the methyl resonances and for temperatures between 273.0 and 333.0 K are displayed in Figure 7, together with a simulation. Two dynamical processes occur. The first, relatively fast one leads to exchange between the inner two resonances as well as exchange between the outer two resonances. One explanation is the fast flipping of the ZnCl$_2$ group from one side of the ligand to the other as sketched in Equation (5).



(5)

In the transition state, the Zn^{II} ion might be coordinated to both imino N atoms. As a result of the line-shape analysis, the Gibbs' free activation energy for this process can be estimated to be $\Delta G^{\ddagger}$ (313 K) = 66 kJ mol^{-1}.[22] In this process both the imino and the amino bond to the Zn^{II} are cleaved. Therefore it is difficult to obtain information on the amino–Zn bond alone from these data. The slower process leads to exchange of the inner signals with the two outer ones. It might correspond to rotations around the N=C imino bonds, which exchange the NEt$_2$ groups of each guanidino moiety. For this process, the Gibbs' free activation energy amounts to ca. $\Delta G^{\ddagger}$ (313 K) = 74 kJ mol^{-1}. A comprehensive study of several dynamic processes within a bis(guanidine)-Pd^{II} complex showed that C=N double bond rotation has the highest Gibbs' free activation energy.[9c]

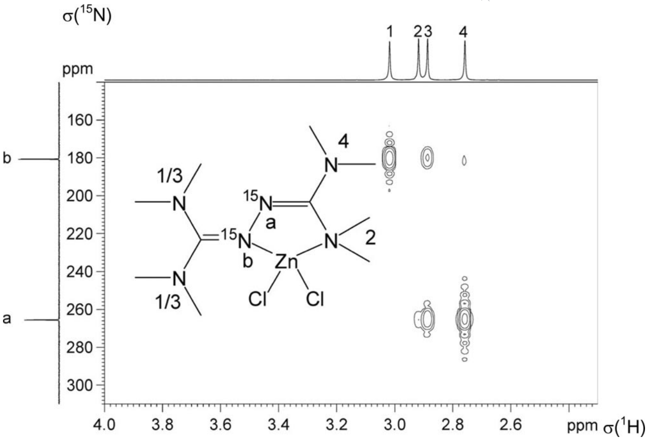


Figure 6. ^{15}N-^{1}H NMR correlation spectrum for **6** in a CDCl$_3$ solution with partially isotopically enriched tmua ligand (^{15}N$_2$-tmua).

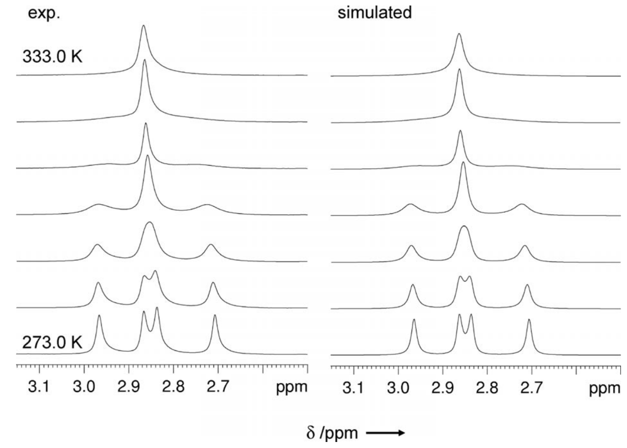


Figure 7. VT ^{1}H NMR spectra (at 200 MHz) for **6** in a CDCl$_3$ solution. Experimental spectrum shown on the left and simulation on the right side.

The NMR spectroscopic data clearly show that the coordinative link to the amino group is relatively stable and does not only occur in the solid state, but also in solution. In additional NMR experiments we studied the effect of solvent variations on the kinetics for these two processes. In Figure 8 the VT ^{1}H NMR spectra of **6** in CDCl$_3$ and CD$_3$CN solutions are compared. If CD$_3$CN is used, the processes proceed faster, and therefore at T = 273 K the methyl groups give rise to four signals in CDCl$_3$ solutions, but still only one in CD$_3$CN solutions. The obvious explanation for this solvent dependence is the stabilisation of the transition state of the dynamical process by solvent (CD$_3$CN) coordination. The CD$_3$CN–Zn bond is weaker than the Zn–amino bond, so that coordination of CH$_3$CN only plays a role in the transition state. In line with the experimental results, quantum chemical (B3LYP) calculations indicate that the gas-phase ligand-substitution reaction sketched in Equation (6) is slightly endergonic (ΔE = 0.4 kJ mol^{-1}, ΔH^0 = 4.7 kJ mol^{-1} and ΔG^0 = 33.5 kJ mol^{-1}), so that the equilibrium lies on the left side.

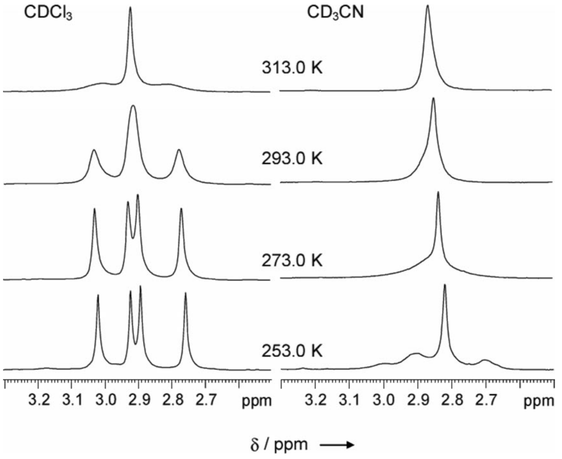
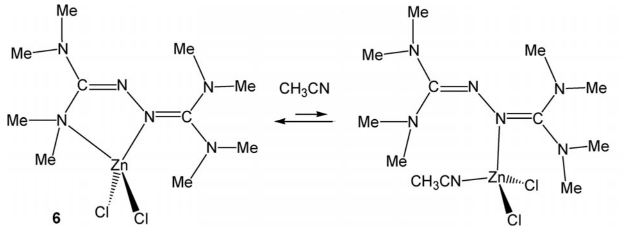


Figure 8. Comparison between the VT ^{1}H NMR spectra (at 200 MHz) recorded for complex **6** in $CDCl_3$ (left side) and in CD_3CN solutions (right side).



(6)

Conclusions

We have discussed several new Zn–guanidine complexes with varying degrees of involvement of the guanidine amino groups in the bonding to the metal. In the complex [(bdmegb)$ZnEt_2$] [bdmegb = 1,2-bis(*N*,*N*′-dimethyl-*N*,*N*′-ethyleneguanidino)benzene], only the imino N atoms are directly bound to the metal ion. This situation changes completely in the complex $[(C_6H_4N)NC(N(H)i\text{Pr})(Ni\text{Pr})ZnMe]_2$, in which deprotonation of one of the guanidino NH*i*Pr groups leads to a strong amido N–Zn bond in addition to imino N–Zn bonding. Finally, in the complexes [(tmua)$ZnEt_2$] and [(tmua)$ZnCl_2$] (tmua = tetramethylurea azine), one of the imino and one of the amino groups are directly bound to the metal ion. VT NMR spectroscopy was used to obtain information about the fluxional processes within the [(tmua)$ZnCl_2$] complex.

The possibility of forming such relatively weak amino coordinative bonds to a metal ion might be of interest for applications in catalysis. Hence the amino group might act as hemilabile ligand, stabilizing a free vacancy at the metal without prohibiting substrate coordination. Preliminary calculations on olefin polymerization reactions with Ni complexes featuring chelating bis(guanidine) ligands indeed point to such an effect.[23] In future work we want to explore the catalytic properties of guanidine complexes making use of the stabilizing effect of the amino groups in model intermediates with free metal vacancies. It also is a subject of ongoing research to synthesize dinuclear metal complexes of tmua, dmeua or related ligands.

Experimental Section

General: All reactions were carried out under purified argon atmosphere and using standard Schlenk techniques. The preparation of bdmegb is detailed in previous work.[15] NMR spectra were measured on a Bruker Avance III 600 spectrometer at a temperature of 23 °C, or a Bruker Avance DPX 200, and referenced to known standards [NH_3(liq.) for ^{15}N shifts]. Elemental analyses were carried out at the Microanalytical Laboratory of the University of Heidelberg. IR spectra were recorded on a Biorad Excalibur FTS3000 spectrometer.

1: 100.1 mg (0.33 mmol) of bdmegb was dissolved in 2 mL THF and 0.3 mL of a 1.5 M $ZnEt_2$ solution in toluene added dropwise. The reaction mixture was stirred for a period of 3 h at room temperature. The solution was layered with *n*-hexane at –20 °C to obtain colourless crystals (99.3 mg, 0.23 mmol, 71 % yield). $C_{20}H_{34}N_6Zn$ (423.93): calcd. C 56.66, H 8.08, N 19.82, Zn 15.43; found C 56.92, H 8.11, N 19.47. ^{1}H NMR (399.89 MHz, CD_2Cl_2, 296 K): δ = 6.72 (m, 4 H, $CH_{\text{arom.}}$), 3.36 (s, 8 H, CH_2), 2.70 (s, 6 H, CH_3), 0.99 (t, 6 H, $CH_{3,\text{Et}}$), –0.33 (q, 6 H, $CH_{2,\text{Et}}$) ppm. ^{13}C NMR (100.55 MHz, CD_2Cl_2, 296 K): δ = 160.72 (CN_3), 142.61 ($C_{\text{q,arom.}}$), 122.33 ($C_{\text{H,arom.}}$), 121.02 ($C_{\text{H,arom.}}$), 49.37 (CH_2), 36.07 (CH_3), 14.39 ($CH_{3,\text{Et}}$), 3.13 ($CH_{2,\text{Et}}$) ppm. IR (CsI disc): $\tilde{\nu}$ = 3050 (w), 2924 (m), 2847 (m), 2698 (w), 1606 (s), 1567 (vs), 1482 (s), 1451 (m), 1408 (m), 1281 (m), 1236 (m), 1204 (w), 1136 (w), 1108 (w), 1074 (w), 1034 (m), 973 (m), 936 (w), 886 (w), 865 (w), 784 (w), 740 (m), 706 (w), 650 (w), 588 (m), 548 (w) cm^{-1}. Crystal data for $C_{20}H_{34}N_6Zn$, *M*r = 423.90, $0.50\times0.45\times0.40$ mm^3, monoclinic, space group $P2_1/n$, a = 13.442(3), b = 11.095(2), c = 15.631(3) Å, β = 114.89(3)°, V = 2114.7(7) Å^3, Z = 4, d_{calc} = 1.331 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 1.68–31.00°. Reflections measd. 13244, indep. 6743, R_{int} = 0.0648. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0400, wR_2 = 0.0931.

2: Dimethylzinc in toluene (2 mL, 2.4 mmol) was added dropwise to a toluene (10 mL) solution of diprgpy (0.26 g, 1.2 mmol). The solution was stirred at room temperature for 18 h. Removal of the volatile components in vacuo afforded a white solid that was crystallized from toluene at –20 °C to afford 0.388 g (0.647 mmol, crystal yield 54 %) colourless cubic crystals. $C_{26}H_{44}N_8Zn_2$ (599.43): calcd. C 52.09, H 7.40, N 18.69; found C 51.95, H 7.43, N 18.42. ^{1}H NMR (399.89 MHz, C_6D_6): δ = 0.00 (s, 3 H, *Me*Zn), 1.02 (d, ^3J = 6.44 Hz, 6 H, Me_2CHNH), 1.11 (d, ^3J = 6.32 Hz, 6 H, Me_2CHNZn), 3.17 (sept, ^3J = 6.28 Hz, 1 H, $Me_2C\mathit{H}$NZn), 3.42 (d, ^3J = 7.59 Hz, 1 H, N*H*), 4.65 (m, 1 H, $Me_2C\mathit{H}$NH), 6.10 (m, 1 H, $C\mathit{H}_{\text{py}}$), 6.80 (m, 1 H, $C\mathit{H}_{\text{py}}$), 6.89 (m, 1 H, $C\mathit{H}_{\text{py}}$), 6.80 (m, 1 H, $C\mathit{H}_{\text{py}}$) ppm. ^{13}C NMR (100.55 MHz, C_6D_6): δ = –13.12 (*Me*Zn), 23.27 (Me_2CHNH), 25.29 (Me_2CHNZn), 44.50 ($Me_2\mathit{C}$HNH), 47.57 ($Me_2\mathit{C}$HNZn), 113.55 ($\mathit{C}H_{\text{py}}$), 112.24 ($\mathit{C}H_{\text{py}}$), 137.66 ($\mathit{C}H_{\text{py}}$), 144.82 ($\mathit{C}H_{\text{py}}$), 159.75 (N=*C*NN), 162.48 ($\mathit{C}H_{\text{py}}$) ppm. IR (KBr): $\tilde{\nu}$ = 3449, 2955, 2870, 2824, 1612, 1566, 1474, 1435, 1404, 1312, 1273, 1173, 1142, 1011, 887, 841, 779, 733, 648 cm^{-1}. Crystal data for $C_{26}H_{44}N_8Zn_2$, *M*r = 599.43, $0.40\times0.40\times0.35$ mm^3, triclinic, space group $P\bar{1}$, a = 8.7590(18), b = 9.4770(19), c = 10.626(2) Å, α = 65.58(3)°, β = 71.17(3)°, γ = 71.70(3)°, V = 743.3(3) Å^3, Z = 1, d_{calc} = 1.339 Mg m^{-3}, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.16–33.14°. Reflections measd.

10173, indep. 5573, R_{int} = 0.0319. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0351, wR_2 = 0.0790.

tmua: To a solution of triethylamine (8.5 mL, 61.3 mmol) in 10 mL acetonitrile 0.15 mL (3.1 mmol) hydrazine hydrate were added at a temperature of 0 °C. Subsequently 2-chloro-1,1′,3,3′-tetramethylformamidium chloride (16.67 mmol), dissolved in 30 mL acetonitrile, were dropwise added and the reaction mixture stirred for a period of 1 h at room temp. The solution was filtered to remove a colourless precipitate of $HNEt_3Cl$, before the solvent was removed under vacuo. The ochre-coloured residue was dissolved in 1 mL 10% aqueous HCl solution. Then 40 mL 25% aqueous NaOH were added and the solution extracted four times with portions of 100 mL CH_2Cl_2. The organic phases were combined and freed from the solvent under vacuo. After sublimation of the crude product under vacuum (10^{-2} mbar) at 90 °C, one obtained 0.5427 g (2.377 mmol, yield 77%) colourless and crystalline product. $C_{10}H_{24}N_6$ (228.35): calcd. C 52.60, H 10.59, N 36.81; obsd. C 52.75, H 10.73, N 36.59. ^1H NMR (399.89 MHz, CD_2Cl_2, 23 °C): δ = 2.83 (s, 12 H), 2.61 (s, 12 H) ppm. $^{13}C\{^1H\}$ NMR (100.55 MHz, CD_2Cl_2, 23 °C): δ = 157.32 (CN_3), 40.53 (CH_3), 40.11 (CH_3) ppm. ^{15}N NMR (60.81 MHz, $CDCl_3$, 23 °C): δ = 239.47 (s, $2N_{\mathrm{azine}}$) ppm. IR (KBr): $\tilde{\nu}$ = 2994 (w), 2916 (m), 2855 (m), 2794 (w), 1575 (vs), 1501 (s), 1452 (s), 1372 (s), 1223 (s), 1332 (m), 1134 (s), 1003 (s), 914 (m), 718 (m), 586 (m), 525 (w) cm^{-1}. HR-EI$^+$: calcd. m/z = 228.2072 for $C_{10}H_{24}N_6$, obsd. m/z = 228.2082 $[M]^+$. EI$^+$: m/z = 228.2 $[M]^+$. Crystal data for $C_{10}H_{24}N_6$, Mr = 228.35, $0.30\times0.30\times0.15$ mm^3, monoclinic, space group $P2_1/c$, a = 8.821(3), b = 8.3920(14), c = 10.443(5) Å, β = 121.41(3)°, V = 659.8(5) Å^3, Z = 2, d_{calc} = 1.149 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.71–32.00°. Reflections measd. 8440, indep. 2287, R_{int} = 0.0702. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0518, wR_2 = 0.1524.

dmeua: To a solution of 18 mL (129 mmol) triethylamine in 50 mL acetonitrile, 0.96 mL (20 mmol) hydrazine hydrate were added at a temperature of 0 °C. Subsequently, 2-chloro-1,3-dimethylimidazolium chloride (47.6 mmol) dissolved in 50 mL of acetonitrile were dropwise added and the reaction mixture stirred for a period of 2 h at room temp. The solution was filtered from the colourless precipitate ($HNEt_3Cl$), before the solvent was removed in vacuo. The orange-coloured residue was dissolved in 4 mL 10% aqueous HCl solution and 75 mL water. After further addition of 100 mL 25% aqueous NaOH solution the mixture was extracted six times with portions of 100 mL CH_2Cl_2. The combined organic phases were freed from the solvent under vacuum. After sublimation of the crude product under vacuum (10^{-2} mbar) at 90 °C, 3.3478 g (14.6 mmol, yield 73%) of colourless and crystalline product were obtained. $C_{10}H_{20}N_6$ (224.32): calcd. C 53.55, H 9.00, N 37.45; obsd. C 53.37, H 8.93, N 37.26. ^1H NMR (399.89 MHz, CD_2Cl_2, 23 °C): δ = 3.26 (s, 6 H, CH_3), 3.09 (s, 4 H, CH_2) 3.08 (s, 4 H, CH_2), 2.61 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100.55 MHz, CD_2Cl_2, 23 °C): δ = 154.92 (CN_3), 51.66 (CH_2), 49.52 (CH_2), 38.73 (CH_3), 35.29 (CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3028 (w), 2926 (m), 2865 (m), 2824 (m), 1611 (vs), 1474 (s), 1428 (m), 1381 (m), 1279 (m), 1260 (s), 1227 (m), 1207 (w), 1139 (w), 1098 (m), 1028 (s), 956 (m), 855 (w), 802 (m), 758 (w), 693 (m), 647 (w), 554 (m) cm^{-1}. HR-ESI: calcd. m/z = 225.18222 for $C_{10}H_{22}N_6$, obsd. m/z = 225.18203 $[M]^+$. Crystal data for $C_{10}H_{20}N_6$, Mr = 224.32, $0.35\times0.35\times0.30$ mm^3, monoclinic, space group $P2_1/c$, a = 7.4950(15), b = 10.694(3), c = 7.508(2) Å, β = 107.33(3)°, V = 574.5(3) Å^3, Z = 2, d_{calc} = 1.297 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 2.85–33.18°. Reflections measd. 2198, indep. 2198, R_{int} = 0.0348. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0398, wR_2 = 0.1099.

3: This compound crystallized in small amounts from THF solutions containing tmua and $ZnCl_2$, which was exposed to air. Crystal data for $C_{10}H_{25}Cl_3N_6Zn$, Mr = 401.08, $0.30\times0.20\times0.20$ mm^3, monoclinic, space group $P2_1/n$, a = 7.3170(15), b = 14.977(3), c = 16.294(3) Å, β = 94.69(3)°, V = 1779.6(6) Å^3, Z = 4, d_{calc} = 1.497 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 1.85–28.69°. Reflections measd. 8986, indep. 4576, R_{int} = 0.0489. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0426, wR_2 = 0.0882.

4: This compound crystallized in small amounts from THF solutions containing dmeua and $ZnCl_2$, which was exposed to air. Crystal data for $C_{10}H_{21}Cl_3N_6Zn$, Mr = 397.05, $0.30\times0.25\times0.23$ mm^3, monoclinic, space group $P2_1/c$, a = 14.966(3), b = 7.2540(15), c = 15.666(3) Å, β = 104.31(3)°, V = 1648.0(6) Å^3, Z = 4, d_{calc} = 1.600 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} 1.40–28.99°. Reflections measd. 8320, indep. 4309, R_{int} = 0.0967. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0562, wR_2 = 0.0992.

5: 75 mg (0.32 mmol) of tmua was dissolved in 1 mL n-hexane and 0.3 mL of a 1.5 M $ZnEt_2$ solution in toluene was added dropwise. The reaction mixture was stirred for a period of 3 h at room temperature. The solution was stored at –20 °C to obtain colourless crystals. Due to the extremely high water and moisture sensitivity, no yield or elemental analysis could be provided. ^1H NMR (399.89 MHz, CD_2Cl_2, 296 K): δ = 2.78 (s, 12 H, CH_3), 2.63 (s, 12 H, CH_3), 1.12 (t, 6 H, $CH_{3,\mathrm{Et}}$), –0.24 (q, 6 H, $CH_{2,Et}$) ppm. ^{13}C NMR (100.55 MHz, CD_2Cl_2, 296 K): δ = 158.05 (CN_3), 40.62 (CH_3), 40.05 (CH_3), 13.92 ($CH_{3,Et}$), 2.16 ($CH_{2,Et}$) ppm. IR: $\tilde{\nu}$ = 2998 (w), 2923 (m), 2872 (m), 2795 (w), 1571 (vs), 1522 (m), 1457 (m), 1430 (m), 1372 (m), 1258 (w), 1228 (w), 1138 (m), 1104 (w), 1053 (w), 1011 (m), 940 (w), 917 (w), 806 (w), 725 (w) cm^{-1}. Crystal data for $C_{14}H_{34}N_6Zn$, Mr = 351.84, $0.50\times0.45\times0.40$ mm^3, monoclinic, space group $C2/c$, a = 15.366(3), b = 15.530(3), c = 16.412(3) Å, β = 103.54(3)°, V = 3807.6(13) Å^3, Z = 8, d_{calc} = 1.228 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, λ = 0.71073 Å), T = 100 K, θ_{range} = 1.89–28.70°. Reflections measd. 9594, indep. 4927, R_{int} = 0.0339. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0476 wR_2 = 0.1126.

6: 0.115 g (0.50 mmol) tmua were dissolved in 10 mL CH_3CN. After dropwise addition of 0.4 mL of a 1 M $ZnCl_2$ solution in Et_2O, the reaction mixture was stirred for a period of 24 h at room temp. The solvent was removed in vacuo and the residue washed three times with 8 mL toluene to remove traces of unreacted tmua. After drying the compound under vacuum 0.1471 g (0.404 mmol, yield 80%) of product were obtained as a colourless powder. The product was recrystallized from CH_3CN solutions at –21 °C. $C_{10}H_{24}Cl_2N_6Zn$ (364.62): calcd. C 32.94, H 6.63, N 23.05, Cl 19.44 Zn 17.94; obsd. C 33.00, H 6.63, N 22.80. ^1H NMR (600 MHz, $CDCl_3$, 0 °C): δ = 2.99 (s, 6 H), 2.89 (s, 6 H), 2.86 (s, 6 H) ppm. $^{13}C\{^1H\}$ NMR (100.55 MHz, $CDCl_3$, 0 °C): δ = 162.60 (CN_3), 154.43 (CN_3), 43.00 (CH_3), 40.50 (CH_3), 40.36 (CH_3), 39.97 (CH_3) ppm. ^{15}N NMR spectroscopic data were recorded with the ligand $^{15}N_2$-tmua. ^{15}N NMR (60.84 MHz, $CDCl_3$, 0 °C): δ = 265.55 (d, ^1J = 9.19 Hz, N_{azine}), 180.72 (d, ^1J = 9.16 Hz, N_{azine}) ppm. In the correlation spectra, the amido ^{15}N nuclei (not enriched) were detected as small signals at δ = 61.5 and 61.0 ppm. IR (KBr): $\tilde{\nu}$ = 3005 (w), 2951 (m), 2873 (m), 2800 (w), 1594 (s), 1570 (vs), 1533 (s), 1466 (m), 1424 (m), 1396 (s), 1359 (m), 1257 (w), 1223 (w), 1181 (w), 1142 (m), 1104 (w), 1059 (w), 1026 (m), 971 (w), 910 (w), 828 (w), 722 (w), 635 (w), 592 (w), 592 (w) cm^{-1}. Crystal data for $C_{10}H_{24}Cl_2N_6Zn$, Mr = 364.62, $0.40\times0.35\times0.35$ mm^3, monoclinic, space group P2(1), a = 9.3670(19), b = 8.1770(16), c = 10.560(2) Å, β = 96.68(3)°, V = 803.3(3) Å^3, Z = 2, d_{calc} = 1.507 $Mg\,m^{-3}$, Mo-K_α radiation (graphite-monochromated, $\lambda = 0.71073$ Å), T = 100 K, θ_{range} = 1.94–29.19°. Reflections measd. 8068, indep. 4282, R_{int} = 0.0329. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0293, wR_2 = 0.0619.

X-ray Crystallographic Study: Suitable crystals were taken directly out of the mother liquor, immersed in perfluorinated polyether oil, and fixed on top of a glass capillary. Measurements were made on a Nonius–Kappa CCD diffractometer with low-temperature unit using graphite-monochromated Mo-K_α radiation. The temperature was set to 100 K. The data collected were processed using the standard Nonius software.[24] All calculations were performed using the SHELXT-PLUS software package. Structures were solved by direct methods with the SHELXS-97 program and refined with the SHELXL-97 program.[25,26] Graphical handling of the structural data during solution and refinement was performed with XPMA.[27] Atomic coordinates and anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares calculations.

CCDC-773976 (for **1**), -773975 (for **2**), -770436 (for tmua), -770437 (for dmeua), -784039 for (for **3**), -784041 (for **4**), -784040 (for **5**), and -770438 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Calculational Details: Quantum chemical calculations were carried out with the TURBOMOLE V.5-9-1 program package.[28] The B3LYP functional [29] in combination with the def2-TZVP basis set were applied.

Supporting Information (see also the footnote on the first page of this article): Comparison between experimentally determined (XRD) and calculated (B3LYP/def2-TZVP) structural parameters for complex **6**, Eyring plots for the dynamic of complex **6**, illustration of the structures calculated for [(tmua)ZnCl$_2$] (**6**) and [(tmua)-ZnCl$_2$(NCMe)].

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