Supporting information

Towards Factors Affecting the Degree of Zinc Alkyls Oxygenation: A Case of Organozinc Guanidinate Complexes

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1. Synthesis and characterization of complexes 1-3

General remarks: All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen, using standard Schlenk and glove-box techniques unless noted otherwise. Di-*tert*-butylzinc[1] and tbo-H proligand[2] were prepared according to the literature procedures. All other chemicals and solvents were purchased from Sigma-Aldrich. Solvents were carefully dried and distilled immediately prior to use. NMR spectra were acquired using the Varian Mercury 400 MHz Spectrometer.

Synthesis of [*t*BuZn(tbo)] (1): A toluene solution of tbo-H (111 mg, 1 mmol) was cooled to -78 ^{o}C and afterwards a 1M solution of *t*Bu_2Zn (1 ml, 1 mmol) in toluene was added dropwise. The reaction mixture was slowly heated to room temperature and stirred for 2 h. Compound **1** was obtained as white solid after evaporation of the solvent. Isolated yield: 221 mg (95 %). Purity of the product was established based on the elemental analysis: C, H ,N (%) calculated for $C_9H_{17}N_3Zn$: C 46.47, H 7.37, N 18.06; found C 47.12, H 7.43, N 17.97. ^{1}H NMR (C_6D_6, 25 ^{o}C): δ 3.77 – 3.56 (4H, NCH_2), 2.76 – 2.62 (4H, NCH_2), 1.54-1.32 (9H, ZnC(CH_3)$_3$) ppm. ^{13}C NMR(C_6D_6, 25 ^{o}C): δ 183.08, 179.19 (CN$_3$), 57.13 – 48.79 (NCH$_2$), 35.48 – 32.49 (ZnC(CH$_3$)$_3$) ppm.

Synthesis of {[*t*BuZn(tbo)]$_2$·[*t*BuOOZn(tbo)]} (2): A solution of **1** (232 mg, 1 mmol) in 5 ml of toluene was cooled to -20 ^{o}C and exposed to atmosphere of pure O_2 for 30 min at -20 ^{o}C. Afterwards O_2 atmosphere was replaced with inert gas (N_2) and the reaction mixture was concentrated to ca. 1 ml and stored in -20 ^{o}C, which resulted in formation of colorless crystals of **2**. Isolated yield: 158 mg (65 %). Purity of the product was established based on the elemental analysis: C, H ,N (%) calculated for $C_{27}H_{51}N_9O_2Zn_3$: C 44.43, H 7.04, N 17.27; found C 44.22, H 6.91, N 17.06. ^{1}H NMR (C_6D_6, 25 ^{o}C): δ 3.85 – 3.57 (12H, NCH_2), 2.77 – 2.61 (12H, NCH_2), 1.55 – 1.32 (27 H, ZnOOC(C*H*$_3$)$_3$ and ZnC(C*H*$_3$)$_3$) ppm. ^{13}C NMR(C_6D_6, 25 ^{o}C): δ 187.97, 183.07, 179.19 (*C*N$_3$), 78.61 (ZnOO*C*(CH$_3$)$_3$), 57.13 – 50.22 (N*C*H$_2$), 35.28 – 27.55 (Zn*C*(*C*H$_3$)$_3$ and ZnOOC(*C*H$_3$)$_3$) ppm.

Synthesis of {[*t*BuZn(tbo)]$_2$·[*t*BuOZn*t*Bu]} (3): A toluene solution of tbo-H (111 mg, 1 mmol) was cooled to -78 ^{o}C and afterwards a 1M solution of *t*Bu$_2$Zn (1 ml, 1 mmol) in toluene was added dropwise. The reaction mixture was slowly heated to room temperature and stirred for 2 h. During this process the reaction mixture was exposed to air at room temperature. Afterwards the reaction mixture was concentrated to ca. 1 ml using vacuum treatment. After keeping the resulting mixture at -20 ^{o}C for 48 h the colorless crystals of **3** were obtained. Isolated yield: 46 mg (21 %). Purity of the product was established based on the elemental analysis: C, H ,N (%) calculated for $C_{26}H_{52}N_6OZn_3$: C 47.25, H 7.93, N 12.72; found C 47.30, H 7.94, N 12.51. ^{1}H NMR (C_6D_6, 25 ^{o}C): δ 3.76 – 3.59 (8H, NC*H*$_2$), 2.76 – 2.63 (8H, NC*H*$_2$), 1.54 – 1.33 (36 H, ZnOC(C*H*$_3$)$_3$ and ZnC(C*H*$_3$)$_3$) ppm. ^{13}C NMR(C_6D_6, 25 ^{o}C): δ 183.04, 181.81, 178.87 (*C*N$_3$), 73.54 (ZnO*C*(CH$_3$)$_3$), 56.68 – 48.70 (N*C*H$_2$), 35.39 – 33.44 (Zn*C*(*C*H$_3$)$_3$ and ZnOC(*C*H$_3$)$_3$) ppm.

2. ^{1}H and ^{13}C NMR spectra of complexes 1-3

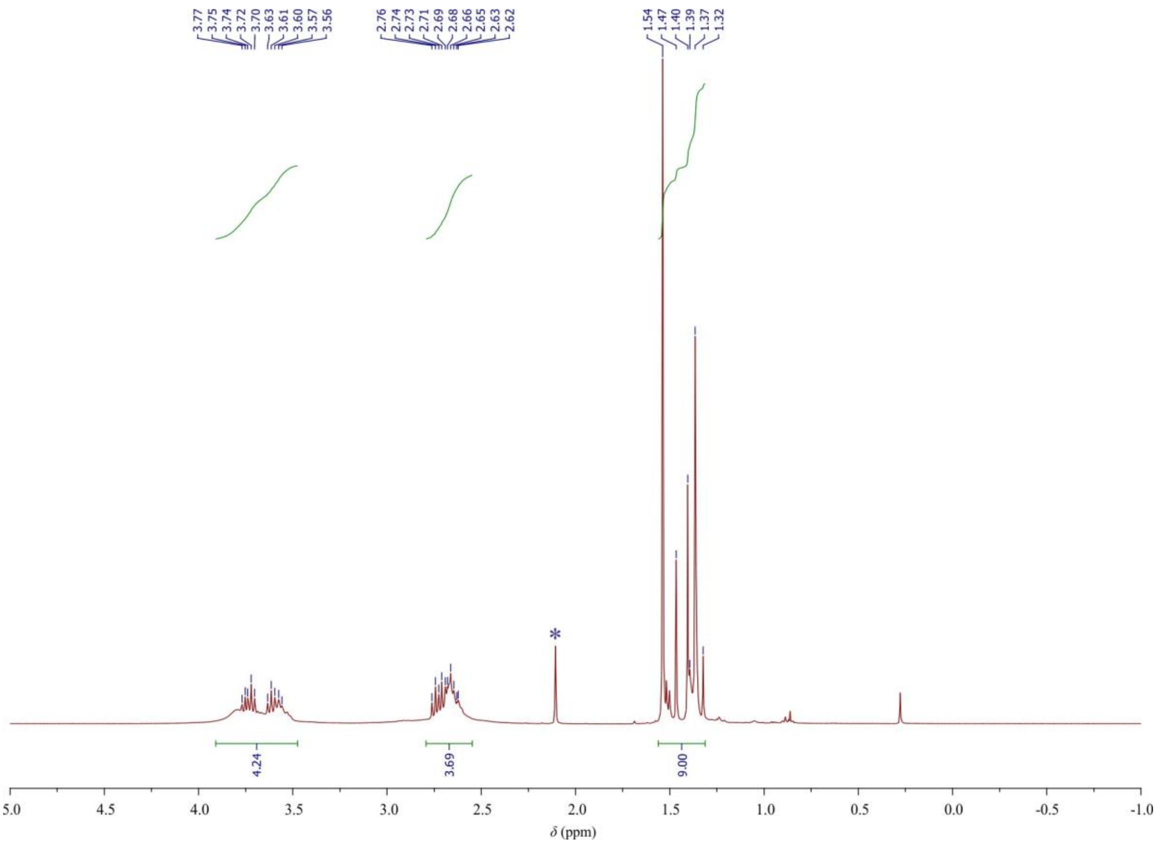

Figure S1. ^{1}H NMR spectrum of complex **1** in C_6D_6 (* = toluene).

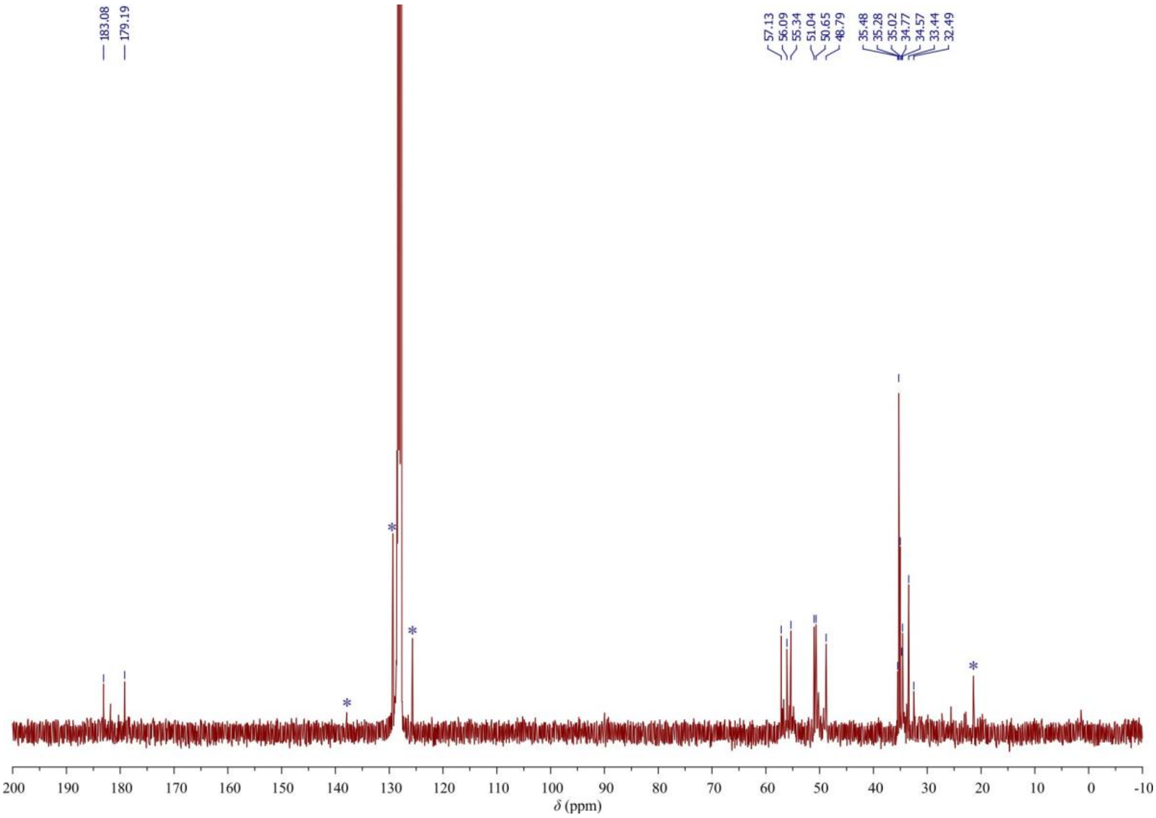

Figure S2. ^{13}C NMR spectrum of complex **1** in C_6D_6 (* = toluene).

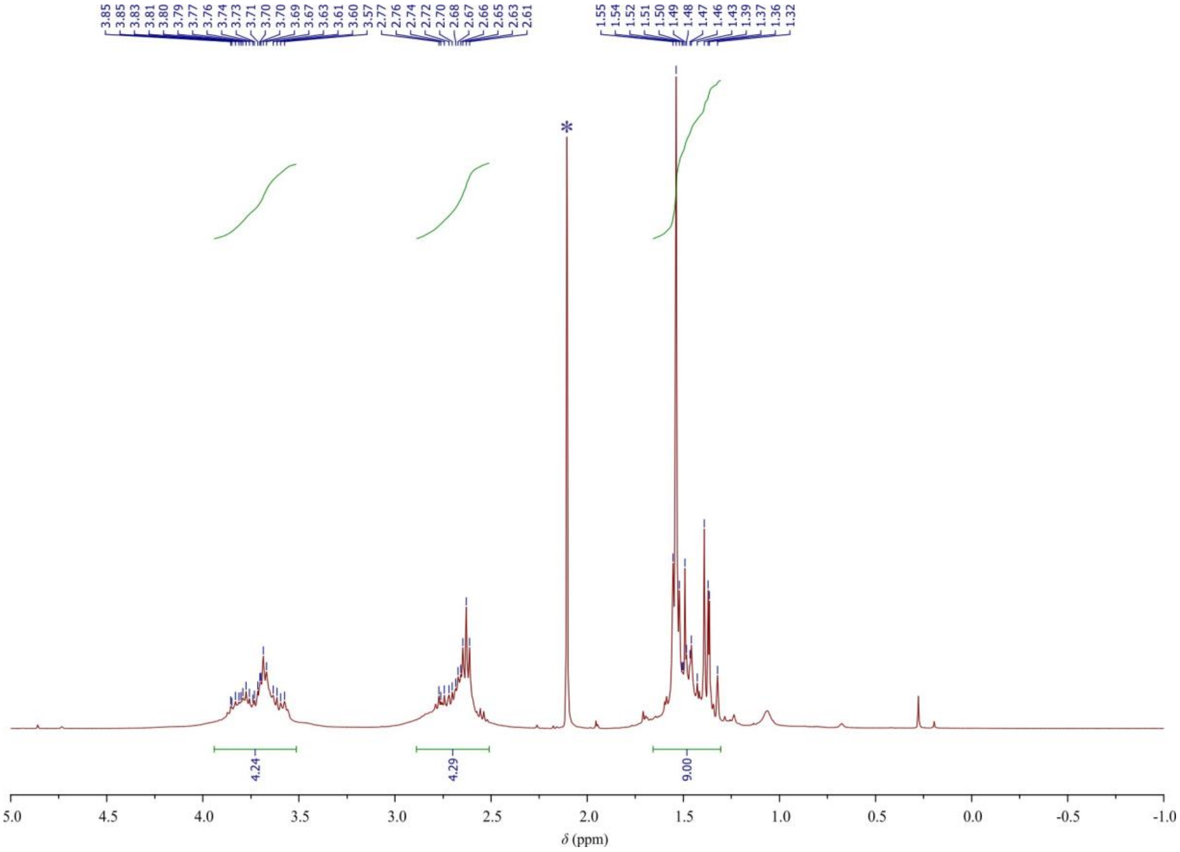

Figure S3. ^{1}H NMR spectrum of complex **2** in C_6D_6 (* = toluene).

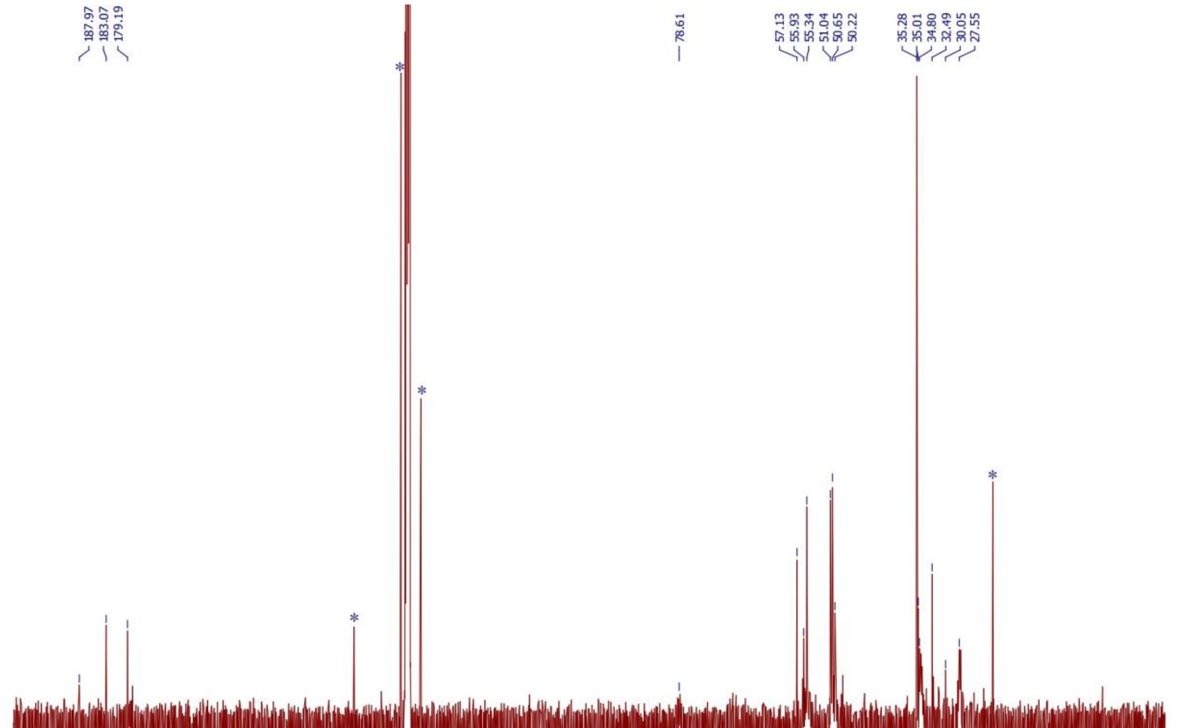

Figure S4. ^{13}C NMR spectrum of complex **2** in C_6D_6 (* = toluene).

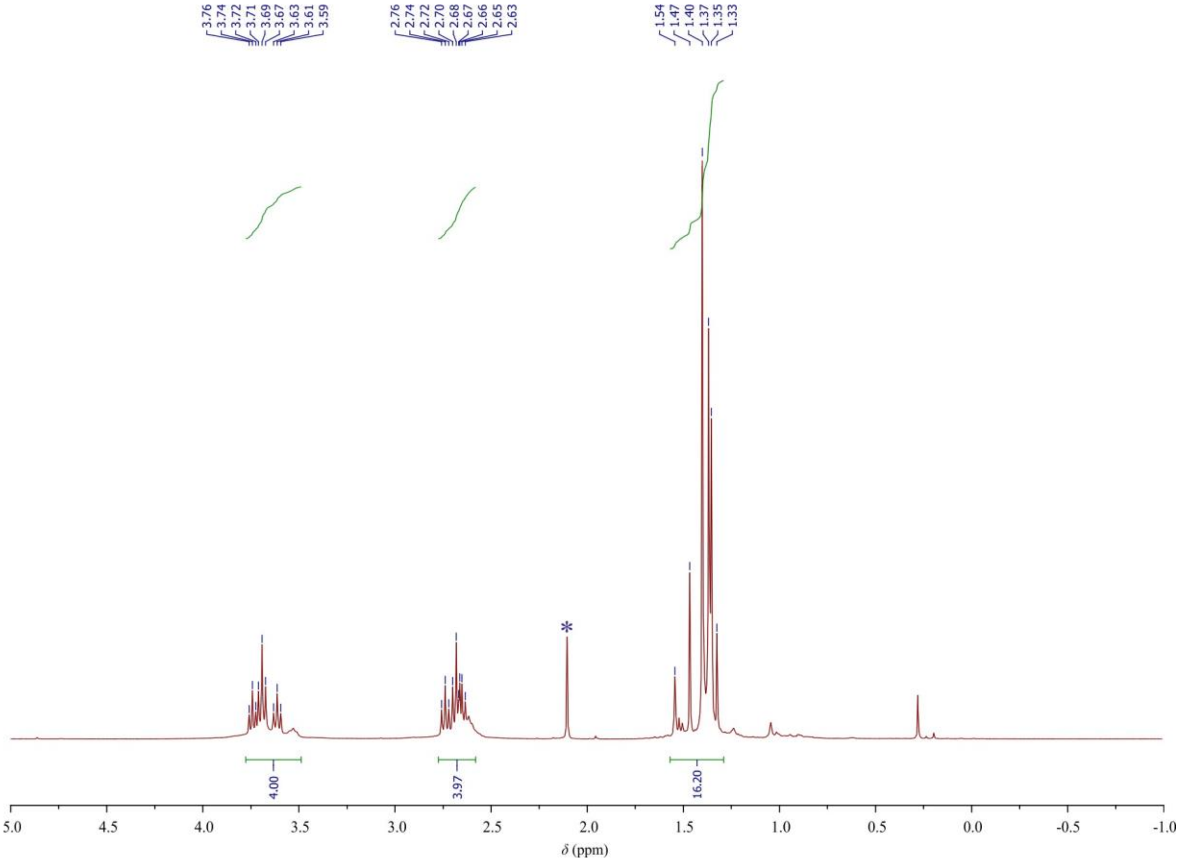

Figure S5. ^{1}H NMR spectrum of complex **3** in C_6D_6 (* = toluene).

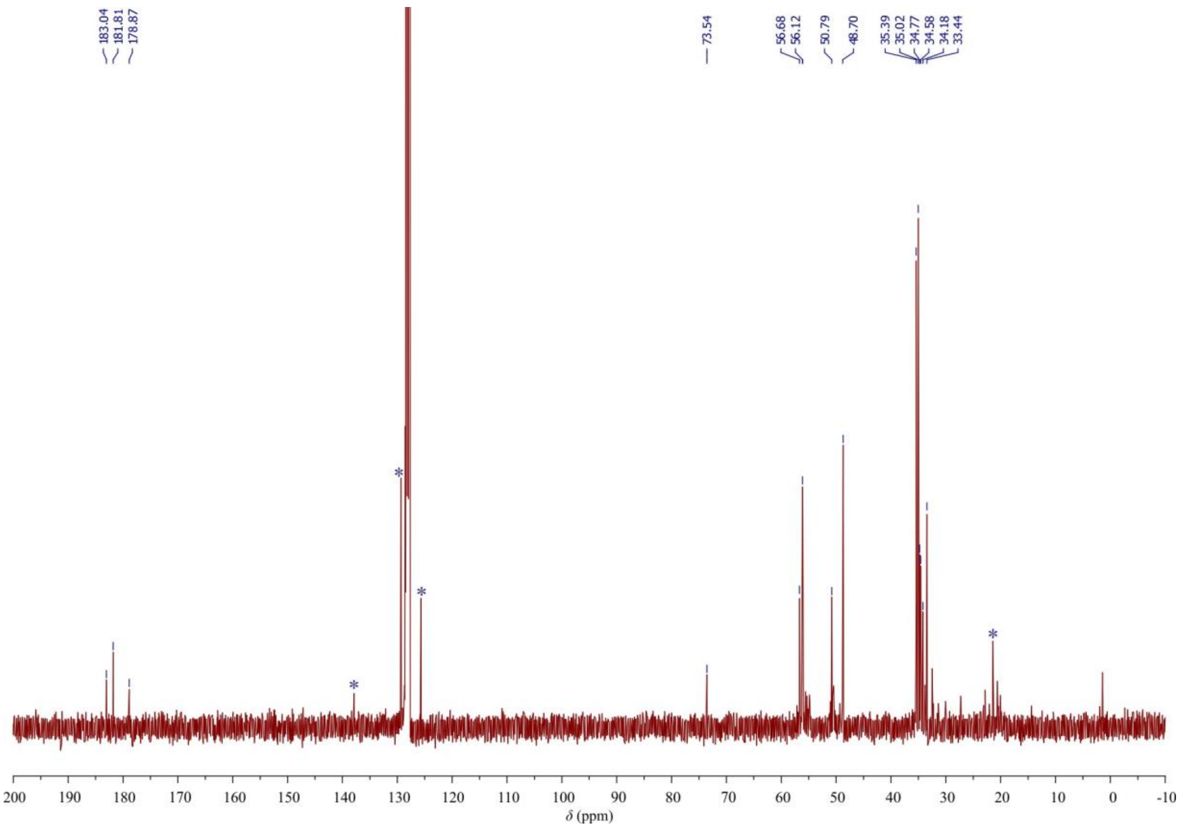

Figure S6. ^{13}C NMR spectrum of complex **3** in C_6D_6 (* = toluene).

3. Crystallographic study of complexes 2 and 3

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes **2** and **3** were collected at 100(2) K on a SuperNova Agilent diffractometer using Mo*Kα* radiation (λ = 0.71073 Å). The data were processed with *CrysAlisPro*.[3] [The structure was solved by direct methods using the SHELXS-97 program and was refined by full matrix least–squares on F^2 using the program SHELXL-97.[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms.

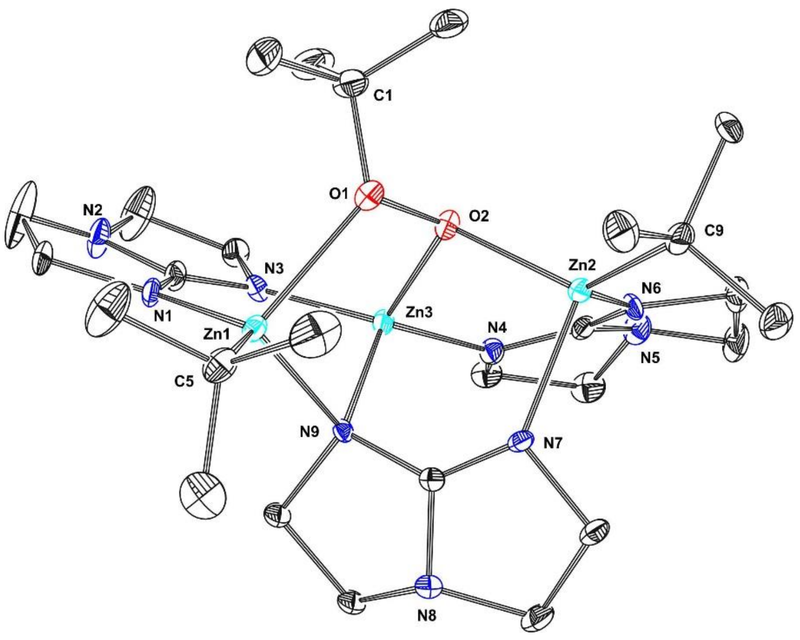

Figure S7. Molecular structure of 2 with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Crystal data for **2**; $C_{27}H_{51}N_9O_2Zn_3$: *M* = 729.88, crystal dimensions 0.32 × 0.16 × 0.10 mm^3, monoclinic, space group *P* 21/n (no. 14), *a* = 15.5234(3) Å, *b* = 11.4166(2) Å, *c* = 19.5381(4) Å, *β* = 105.759(2) °, *U* = 3332.48(11) $Å^3$, *Z* = 4, *F*(000) = 1528, D_c = 1.455 g cm^{-3}, K, *μ(*Mo-K*α*) = 2.180 mm^{-1}, θ_{max} = 29.215 °, 7612 unique reflections, *R*1 = 0.0865, *wR*2 = 0.1128 for all data and 379 parameters and 0 restraints, $R1 = 0.0544$, $wR2 = 0.0990$ for 5102 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 0.942. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 1.16 /-0.79 eÅ^{-3}.

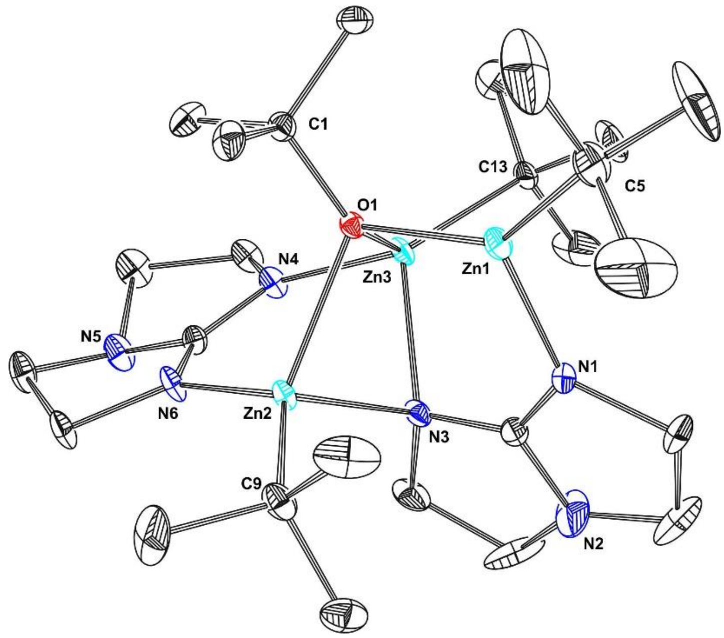

Figure S8. Molecular structure of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Crystal data for **3**; $C_{26}H_{52}N_6OZn_3$: $M = 660.84$, crystal dimensions 0.34 × 0.24 × 0.12 mm^3, monoclinic, space group *C*c (no. 9), $a = 15.3411(8)$ Å, $b = 35.0817(4)$ Å, $c = 9.6154(5)$ Å, $\beta = 142.757(12)$ °, $U = 3131.8(6)$ Å^3, $Z = 4$, $F(000) = 1392$, $D_c = 1.402$ g cm^{-3}, μ(Mo-Kα) = 2.307 mm^{-1}, $\theta_{max} = 29.279$ °, 6464 unique reflections, $R1 = 0.0358$, $wR2 = 0.0795$ for all data and 338 parameters and 2 restraints, $R1 = 0.0334$, $wR2 = 0.0783$ for 6222 reflections with $I_o > 2\sigma(I_o)$. The goodness-of-fit on F^2 was equal 1.076. A weighting scheme $w = [\sigma^2(F_o^2 + (0.0418P)^2 + 3.1964P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$ was used in the final stage of refinement. The residual electron density = + 0.77 /-0.54 eÅ^{-3}.

4. DOSY NMR measurements of complex 1

Diffusion Ordered Spectroscopy (DOSY) was applied for estimation of the size of species of **1** existing in the solution. As demonstrated in literature,[5] molecular weight can be determined based on the combination of Stokes-Einstein equation: $D = (kT) / (6\pi\eta r_H)$ and the relationship between molecular weight M and molar radius: $M = (4\pi r_M^3 \rho N_A)/3$, where r_H and r_M are hydrodynamic and molar radii respectively, η is viscosity and ρ is density of the liquid.

It should be noted, that such estimations lead to substantial errors in the range of 10-20%, unless internal standards are used. Nevertheless, this is accurate enough for the purposes of assessing the aggregation state of typical metalorganic complexes. DOSY experiment was performed using a diluted solution of **1** in deoxygenated toluene-d8. The sample was assumed to retain the physical properties of the pure solvent. Raw data were processed using the DOSY Toolbox software, which is described in detail in the author's publication.[6] Results of the experiment were summarized in Table S1.

Table S1. Diffusion coefficients of **1** and $\mathbf{1_2}$, estimated hydrodynamic radii (r_H) and molecular weights (MW)

Formula	MW_{calcd} [g/mol]	$D \cdot 10^{10}$ [m^2/s]	r_H [Å]	MW_{exp} [g/mol]
[*t*BuZn(tbo)] (**1**)	232.4	7.22	5.0	298
[*t*BuZn(tbo)]$_2$ ($\mathbf{1_2}$)	464.8	6.11	5.9	492

5. References

(1) Lehmkuhl, H.; Olbrysch, O. *Justus Liebigs Ann. Chem.* **1975**, *1975*, 1162–1175.

(2) Cotton, F. A.; Murillo, C. A.; Wang, X.; Wilkinson, C. C. *Inorg. Chem.* **2006**, *45*, 5493–5500.

(3) Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b

(4) Sheldrick, G. M. *Acta Cryst.* **2007**, *64A*, 112–122.

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