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Zinc Complexes of Amine Mono(phenolate) [NOO_2] Ligands: Controlling Coordination Modes by Bulk of Phenolate Substituents

Stanislav Groysman,[a] Ekaterina Sergeeva,[a] Israel Goldberg,[a] and Moshe Kol*[a]

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The coordination chemistry of three tripodal monoanionic amine mono(phenolate) ligands bearing two methoxy sidearm donors with ethylzinc(II) is reported. Reacting diethylzinc with the ligand precursor bearing bulky (*t*Bu) phenolate substituents led cleanly to a mono(ethyl) mononuclear C_s-symmetric zinc complex according to spectroscopic data. X-ray structure analysis revealed a semi-pentacoordinate complex as one of the methoxy sidearm donors was tightly bound whereas the other one was weakly bound. The ligand precursors bearing less bulky electron-donating (Me) or electron-withdrawing (Br) phenolate substituents led cleanly to dinuclear pentacoordinate complexes, bridged by phenolate oxygens, in which only one of the two sidearm donors was bound, and in a weak manner.

Introduction

Zinc plays a major role in bioinorganic chemistry, fulfilling structural and catalytic functions in various enzymes.[1,2] When coordinated by S-based (cysteinate) ligands, or by a mixed set of S- and N-based (histidine) ligands, the role of zinc is mainly structural.[2] On the other hand, a coordination sphere containing O-based ligands is characteristic for a catalytic metal site, as the O-based hard donors (H_2O or HO^-) are readily replaced at the zinc metal center, providing a vacant coordination site to be occupied by a substrate.[2] According to these general observations, simple analogues of the zinc biological active sites are sought.

In such research, controlling the nuclearity of metal species is a major goal. For many applications, mononuclear species are desired, as they lead to better-defined catalytic performance in comparison to multinuclear species. The most practical route toward such species is the utilization of chelating multidentate ligands such as the "tripodal" ligands, having three donor arms, which have become very abundant in the last two decades.[3] One particular family of tripodal ligand, that attracts ever-increasing attention, is the family of tripodal ligands possessing a central nitrogen donor atom, in addition to the three donor arms. Several ligand families of this type have been employed in zinc chemistry, including neutral tris(picolyl)amine ([NN_3]),[4,5] *N*-bis[2-(methylthio)ethyl]-*N*-[(6-neopentylamino-2-pyridyl)-methyl]amine ([NS_2N]),[6] and tris[(*N*-*tert*-butylcarbamoyl)-methyl]amine ([NN_3]) ligands,[7] or monoanionic dipicolylglycinate ([NON_2]),[8] and 2-mercaptobenzyl-bis(2-pyridylmethyl)amine ([NN_2S]) ligands [9] (Figure 1).

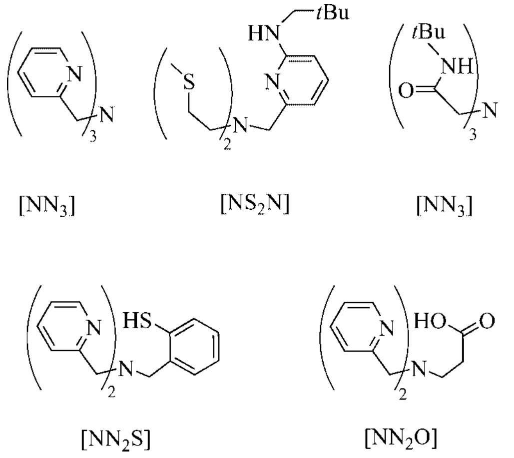

Figure 1. Various tripodal ligands, having a central nitrogen donor employed in zinc chemistry.

The zinc chemistry of monoanionic amine mono(phenolate) ligands, carrying two additional arms, has been investigated in the last decade, mainly by the groups of Fenton and Vahrenkamp.[10–13] The advantages of the amine mono(phenolate) ligands include their straightforward synthesis, and their broad structural diversity.[10–17] Yet, until now, the zinc chemistry of these ligands was limited to ligands having two additional pyridine arms,[10–12] or pyridyl and pyrrolidinyl arms (Figure 2).[13] The [$NON^{py}{}_2$] ligands, having no substituents, or *t*Bu substituents at the phenolate ring, were shown to bind the metal firmly through all four donors, with the three "tripodal" donors lying in the equatorial plane.[11,12] Both ligands led to neutral mononuclear complexes, possessing an additional, monodentate ligand in

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[a] School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel Aviv University,
Tel Aviv 69978, Israel
E-mail: moshekol@post.tau.ac.il

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the fifth position: Cl, Br, I, OPh, and SPh. In this study, we were aiming at extending the chemistry of tripodal monoanionic [NOX_2] ligands. Specifically, we wanted to reveal structural effects on coordination chemistry of [NOO_2]-zinc complexes, in which zinc binds to labile oxygen donors.

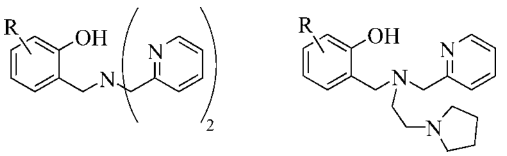
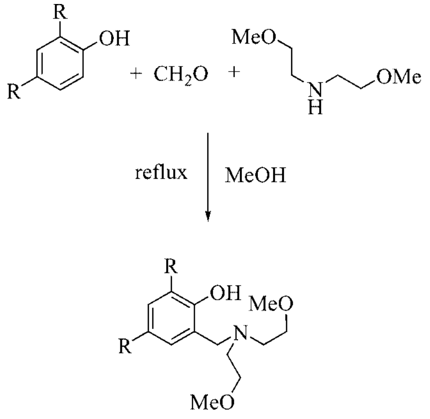


Figure 2. Two tripodal amine mono(phenolate) ligands, employed in zinc chemistry.

Results and Discussion

We previously reported the preparation of the ligand precursor Lig^1H.[17] Lig^2H and Lig^3H ligand precursors were prepared in a similar way, via a single-step Mannich condensation between the respective phenol, secondary amine, and formaldehyde (Scheme 1). The ligand precursors were obtained as yellow oils, and their identity was confirmed by NMR and elemental analyses.



Lig^1H: R = tBu; Lig^2H: R = Me; Lig^3H: R = Br

Scheme 1. Synthesis of ligand precursors Lig^1H–Lig^3H.

Diethylzinc provides a convenient entry into zinc chemistry with sufficiently acidic ligands.[18,19] An ethereal solution of Lig^1H was added to a hexane solution of diethylzinc at –30 °C, followed by warming to room temperature and stirring for 1 h. Subsequent removal of solvent and recrystallization from pentane led to pure **1** in 80% yield, obtained as colorless crystals. According to its NMR spectra, **1** contains a single type of phenolate ring, and a single type of metal-bound ethyl group. As anticipated, the zinc-bound methylene group gives rise to high-field NMR signals [$\delta(^{13}C)$ –1.8 ppm; $\delta(^1H)$ 0.58 ppm]. The ^1H and ^{13}C NMR spectra of this compound clearly signify a C_s-symmetrical species at room temp. Thus, the ^1H spectrum featured a single resonance for the OCH_3 groups at δ = 2.85 ppm [$\delta(^{13}C)$ 58.7 ppm], and a sharp singlet for the two benzyl ($ArCH_2N$) protons at δ = 3.31 ppm (these groups are reflected by a mirror plane). The NCH_2CH_2OMe protons appear as four distinct signals, of ddd (or dt) multiplicity, whose connectivity pattern was validated by a 2D $^1J_{C,H}$ (HMQC) experiment. This indicates that all four methylene protons of a particular "sidearm" are different; thus, the ligand seems to wrap around the metal in a well-defined fashion, in which the two sidearms are reflected by a mirror plane. However, the possibility of a fast (on the NMR timescale) exchange process, in which only one of the sidearms is bound at a given time, cannot be excluded a priori.

To distinguish between these two possibilities, we carried out a VT NMR experiment for **1** in [D_8]toluene. For the latter scenario, two different sidearms should be observed at low temperatures. In contrast, for the compound containing an effective mirror plane, no significant difference between proton spectra at room temp. vs. low temperatures should be anticipated. Upon cooling to as low as 210 K, no splitting in the peak attributed to the OCH_3 groups was observed; the NCH_2CH_2OMe appeared as four distinct signals as well, though all signals were somewhat broadened. The signals attributed to the ethyl group also underwent no change. This data is consistent with a C_s-symmetrical complex in solution, featuring binding of both sidearms (Figure 3). The slight broadening of peaks is attributed to a low-barrier conformational flip of the methylene-phenolate group. A freezing of this flip would result in a C_1-symmetrical complex, as revealed from the X-ray structure of **1**. The X-ray structure also reveals different MeO–Zn bond lengths (vide infra).

The complex of the nonbulky [NOO_2] electron-donating ligand Lig^2 was prepared in a similar way, by a protonolysis reaction between the ligand precursor Lig^2H and Et_2Zn (Figure 3). Complex **2** was obtained as colorless crystals upon recrystallization from ether. Even at room temp. the NMR spectrum of **2** in deuteriobenzene displays different features: the methylene NCH_2CH_2OMe protons appear as two broad signals vs. four sharp signals of ddd (dt) multiplicity for **1** (Figure 3). The OCH_3 protons appear as a single resonance at δ = 2.85 ppm at room temp. and the ethyl group gives rise to single triplet and quartet resonances, at δ = 0.39 and 1.56 ppm, respectively. However, in contrast to **1**, cooling **2** to 210 K causes splitting of the OCH_3 resonance into two discrete signals (coalescence at 221 K). The quartet signal attributed to the metal-bound methylene was split into two multiplets at that temperature as well, signifying a different chemical environment for the two methylene protons. Thus, a different binding of the nonbulky [NOO_2] ligand to the metal should be anticipated, according to the VT-NMR spectroscopic data (Figure 3).

The X-ray structure determination of these complexes provided a solid evidence for the different coordination modes of these [NOO_2] ligands around zinc. According to our expectations for the structure of **1**, the ligand is bound to the metal through all four donors, forming a mononuclear, pentacoordinate species of highly distorted TBP geometry (Figure 4, Table 1). In the previously disclosed zinc complexes featuring the [$NO(N^{py})_2$] ligand,[11,12] the three

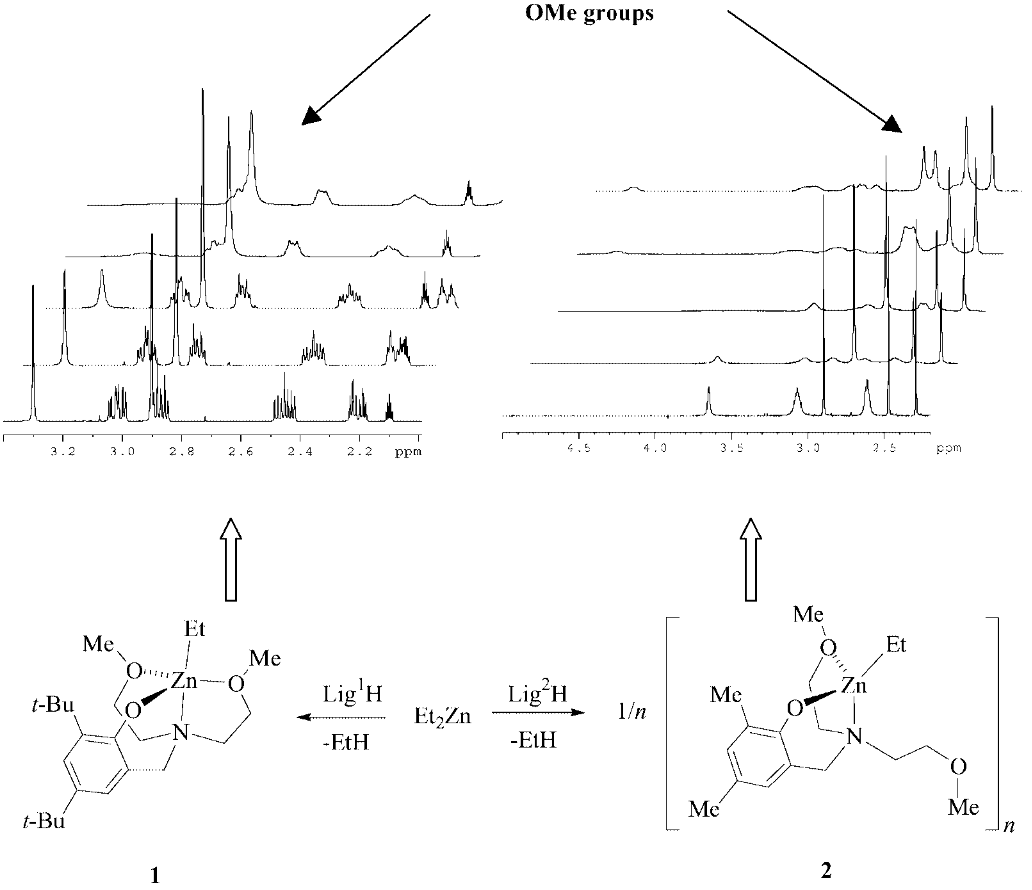


Figure 3. Syntheses of the amine mono(phenolate) complexes **1** and **2**, and their proposed structures; (bottom), based on VT ^1H NMR spectra (top). See text for details.

arms of the tripodal ligand occupied the equatorial positions, while the central amine and the additional monodentate ligand were located in the axial positions. In the present case, the phenolate oxygen, the central nitrogen, and the ethyl methylene carbon are located in the equatorial plane, whereas the methoxy donors occupy the axial positions. The phenolate oxygen, amine donor, and the ethyl methylene carbon all feature strong bonding to the metal center. In contrast, the two methoxy groups are inequivalent, displaying weak binding to the metal: 2.308 vs. 2.598 Å. The pronounced difference in bond lengths may result from the conformation of the ethyl group, as its methylene carbon points toward the remote methoxy group, or from the conformation of the phenolate ring, as the *t*Bu group points toward that group as well, or by a combination of both. It may also signify an "arrested" dynamic process equilibrating bound and unbound sidearm donors. The Zn–O–C(Ph) angle is narrow (114.9°), as is anticipated for a d^{10} metal complex experiencing no π-donation from the phenolate oxygen to the metal, vs. 128–148° in d^0 or d^2 (Ta^V, V^{III}, V^V, or Ti^{IV}) complexes.[20–22]

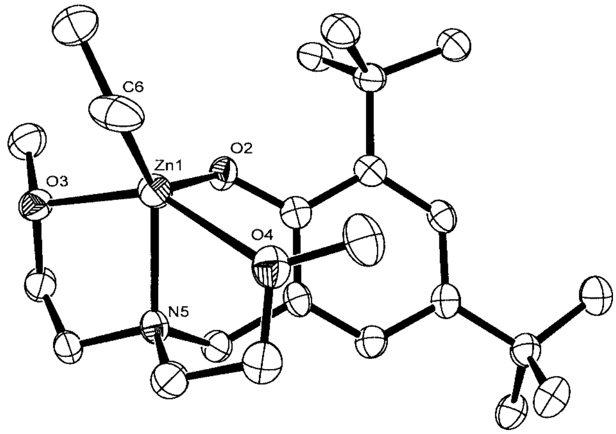


Figure 4. The X-ray structure of **1**. ORTEP representation, 50% probability.

In a sharp contrast to the structure of **1**, **2** is a dinuclear complex of C_i-symmetry, in which the two nearby zinc atoms (Zn···Zn separation of 3.108 Å) are bridged by the two phenolate oxygen atoms (Figure 5, Table 1). This Zn_2O_2 core is a common structural motif in zinc coordination chemistry, found frequently in zinc-phenolate species.[23–27] The Zn–O(Ph) bond lengths are not identical, being 2.018 and 2.123 Å, respectively. One of the sidearms is unbound, creating a pentacoordinate, nearly TBP geometry at each metal center. One of the phenolate oxygen atoms and the methoxy donor are in the axial position [O(Ph)-Zn-

Table 1. Bond lengths [Å] around Zn in the solid-state structure of **1**, **2**, and **3**.

	1	**2**	**3**
Zn1–O2	1.931(2)	2.018(2)	2.036(5)
Zn1–O2′		2.123(2)	2.143(4)
Zn1–O3	2.308(2)	2.549(3)	2.451(5)
Zn1–O4	2.598(2)		
Zn1–N5	2.150(2)	2.169(3)	2.155(6)
Zn1–C6	1.962(2)	1.986(4)	1.975(7)

(R)OMe 159.0°], whereas the second phenolate oxygen, the ethyl methylene carbon, and the central nitrogen are in the equatorial positions. Consistently with the previous structure, the central amine is bound tightly (2.169 Å), and the methoxy donor is bound very weakly (2.549 Å).

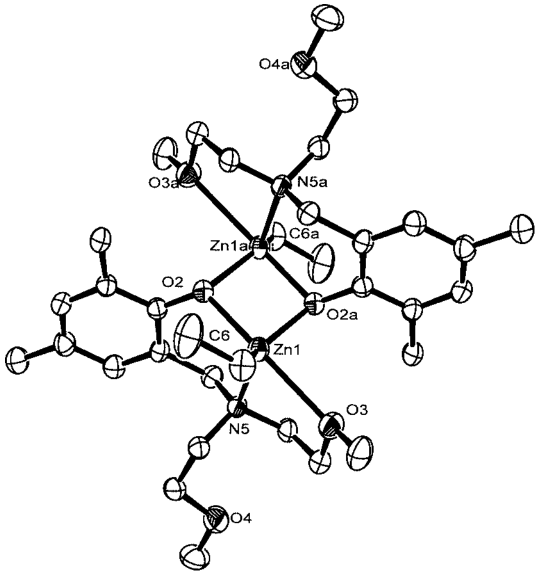


Figure 5. The X-ray structure of **2**. ORTEP representation, 40% probability. The asymmetric unit contains only half of the *Ci*-symmetric dimer, and the second half is generated by a symmetry operation. The structure also contains a disordered solvent molecule, not shown here.

An additional ligand, employed in this research, was Lig^3, carrying *ortho*, *para* bromo substituents, that are comparable in size to the methyl groups, yet are electron-withdrawing and may reduce the tendency of the phenolate oxygen atoms to act as bridging groups. The ligand precursor Lig^{3}H was treated with diethylzinc in analogy to Lig^{1}H and Lig^{2}H; the product **3** was obtained in a good yield after washing out of the impurities with pentane and ether. In general, the room temp. ^{1}H NMR spectrum of **3** displays similar features to that of **2**. In both cases, the NCH_2CH_2O methylene protons give rise to two resonances: For **2**, these are represented by two broad peaks; for **3**, one of these signals is broad, while the second appears as a relatively sharp triplet. The VT NMR behavior of **3** was not identical to the spectrum of **2**: for example, the methylene NCH_2CH_2O protons were observed in **2** at 278 K as four broad multiplets, while in **3** they gave rise to two broad signals at that temperature. Moreover, in spite of a significant broadening in the OCH_3 and Zn-CH_2 resonances, no splitting was observed down to 200 K, which may indicate a lower-energy process in **3** than in **2**; it does not exclude, however, the possibility of a mononuclear, nearly C_s-symmetrical complex.

The X-ray structure analysis provided a clear evidence for the dinuclear nature of **3** (Figure 6). In the solid state, the *Ci*-symmetric **3** possesses a very similar structure to that of **2**, displaying two pentacoordinate metal centers in close proximity (Zn···Zn separation of 3.163 Å), bridged by the phenolate oxygen atoms. The bond lengths in **3** are reminiscent of those in **2**; the major structural difference between these structures lies in the Zn–O(R)Me bond lengths [2.451(5) in **3** vs. 2.549(3) Å in **2**]. The stronger bonding of the weak donor in **3** may be traced back to the electron deficiency at the metal center, as a result of the electron-poor ligand.

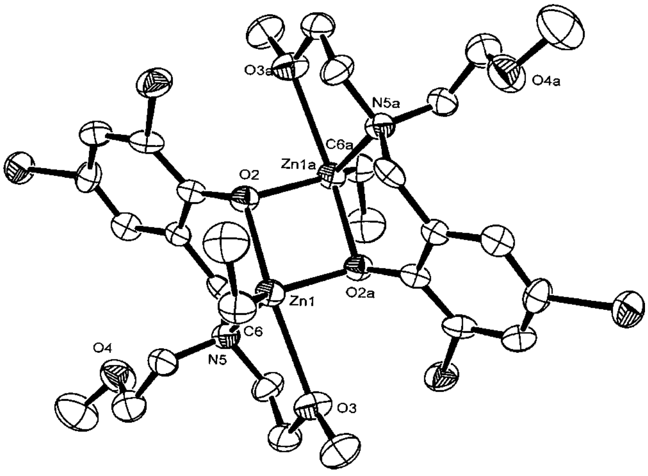


Figure 6. The X-ray structure of **3**. ORTEP representation, 40% probability. The asymmetric unit contains only half of the *Ci*-symmetric dimer, and the second half is generated by a symmetry operation.

On the basis of the above results, we propose that a point of divergence for the different nuclearity in [NOO_2]ZnEt species lies in a delicate balance between the weakness (lability) of the dative Zn–O(R)Me bond and the steric bulk imposed by the groups in the *ortho* positions of the phenolate ring. Presumably, formation of a dinuclear phenolate-bridged species in the [NOO_2] zinc complexes is favorable due to the weakness of the Zn–O(R)Me dative bond. However, the formation of dinuclear species is precluded by sufficient steric bulk at the *ortho* positions of the phenolate group.[28] As a result, mononuclear species arise, in which the weak, yet nonbulky, second O(R)Me donor is able to bind to the metal center, accomplishing a pentacoordinate geometry.

To summarize, we investigated the coordination chemistry of zinc(II) in the environment of the amine mono(phenolate) ligands, carrying two neutral oxygen-type arms, in addition to the anionic phenolate oxygen. A neutral oxygen donor, known to bind weakly to zinc, was found to display varying coordination modes, influenced by the steric bulk at the phenolate ring. In the case of small groups at the phenolate ring, formation of a dinuclear complex was observed, in which every metal atom was bound to two phenolate oxygen atoms, at the expense of binding of a second weak donor. In contrast, utilization of bulkier, *t*Bu, groups at the phenolate ring prohibited the formation of a dinuclear complex, leading to a mononuclear species instead, in which both neutral oxygen donors were bound.

Experimental Section

General: All manipulations of the metal complexes were performed under dry nitrogen in a nitrogen-filled glovebox. 2,4-Di-*tert*-butylphenol, bis(2-methoxyethyl)amine, formaldehyde (37% in water), and diethylzinc (1.0 M in hexane) were obtained from Aldrich and used without purification. Lig^{1}H was prepared as described previously.[17] Ether was purified by reflux and distillation under dry Ar from Na/benzophenone. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from Na/benzophenone. [D$_6$]-Benzene was flushed with Ar and stored on molecular sieves in the glovebox. [D$_8$]Toluene was dried on Na before being used. NMR spectroscopic data for the metal complexes were collected with Bruker AC-200 and AC-400 spectrometers, and referenced to protio impurities in [D$_6$]benzene and [D$_8$]toluene (δ = 7.15 and 2.1 ppm, respectively) and to the ^{13}C chemical shift of benzene (δ = 128.06 ppm). Routine characterization of metal complexes consisted of ^{1}H, BB, and DEPT-135 ^{13}C NMR experiments, performed in [D$_6$]benzene at 298(2) K. VT NMR experiments were performed in [D$_8$]toluene. X-ray diffraction measurements were performed with a Nonius Kappa CCD diffractometer system, using Mo-K_α (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to 110 K. The structures were solved by a combination of direct methods and Fourier techniques using SIR-92 software,[29] and were refined by full-matrix least-squares with SHELXL-97.[30] The crystal and experimental data are summarized in Table 2. CCDC-294424 (for **1**), -294425 (for **2**), and -294426 (for **3**) 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. Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem.

Table 2. Crystallographic experimental details.

	1	**2**	**3**
Formula	$C_{23}H_{41}NO_3Zn$	$C_{17}H_{29}NO_3Zn$	$C_{15}H_{23}Br_2NO_3Zn$
fw	444.94	360.78	490.53
a [Å]	9.4730(6)	26.8350(7)	10.4670(5)
b [Å]	9.8160(6)	26.8350(7)	9.2700(6)
c [Å]	13.890(1)	10.6420(3)	18.1480(10)
α [deg]	82.162(4)	90.00	90.00
β [deg]	69.988(3)	90.00	93.036(4)
γ [deg]	81.258(4)	90.00	90.00
Crystal system	triclinic	tetragonal	monoclinic
Space group	$P\bar{1}$	$I4_1/a$	$P2_1/c$
V [Å^3]	1194.55(14)	7663.5(4)	1758.41(17)
D_c [g cm^{-1}]	1.237	1.251	1.853
μ [cm^{-1}]	1.049	1.293	5.952
Z	2	16	4
No. of measd. reflns.	5559	4543	3226
No. of reflns. [$I > 2\sigma(I)$]	3890	3307	2205
R_1 [$I > 2\sigma(I)$]	0.0524	0.0534	0.0546
wR_2 [$I > 2\sigma(I)$]	0.1104	0.1498	0.1163
GOF	1.003	1.042	1.010

Synthesis of Lig^{2}H: 2,4-Dimethylphenol (5.5 mL, 46 mmol), bis(2-methoxyethyl)amine (13 mL, 89 mmol), and formaldehyde (13 mL, 37% in water) were mixed in MeOH (20 mL). The mixture was heated to 110 °C in a pressure flask and stirred for 48 h, yielding a deep orange biphasic solution. The crude reaction mixture was poured into water/CH_2Cl_2 (40 mL each), the organic phase was separated, dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The traces of amine were removed under vacuum (0.5 mbar), while heating to 80 °C, yielding the desired product as orange oil (9.243 g, 35 mmol, 76%). $C_{15}H_{25}NO_3$ (267.36): calcd. C 67.38, H 9.42, N 5.24; found C 67.31, H 9.71, N 5.44. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 10.32 (s, 2 H, O-*H*), 6.74 (br. s, 2 H, Ar-H), 6.52 (br. s, 2 H, Ar-H), 3.69 (s, 2 H, ArC*H*$_2$N), 3.43 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H, NCH$_2$C*H*$_2$O), 3.23 (s, 6 H, OC*H*$_3$), 2.70 (t, $^3J_{H,H}$ = 5.5 Hz, 4 H, NC*H*$_2$C*H*$_2$O), 2.11 (s, 6 H, Ar-C*H*$_3$) ppm. ^{13}C NMR (50.29 MHz, $CDCl_3$): δ = 153.7 (*C*O), 130.6 (*C*H), 127.6 (*C*), 126.9 (*C*H), 124.8 (*C*), 121.5 (*C*), 70.5 (*C*H$_2$), 58.8 (O*C*H$_3$), 58.6 (*C*H$_2$), 53.4 (*C*H$_2$), 20.5 (*C*H$_3$), 15.8 (*C*H$_3$) ppm.

Synthesis of Lig^{3}H: 2,4-Dibromophenol (1.97 g, 7.8 mmol), bis(2-methoxyethyl)amine (2 mL, 13.6 mmol), and formaldehyde (3.2 mL, 37% solution in water) were mixed in MeOH (20 mL). The mixture was stirred and refluxed for two weeks. The crude reaction mixture was poured into water/CH_2Cl_2 (20 mL each), the organic phase was separated, dried with anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The remaining product was dried (0.5 mbar, 100 °C) for 2 h, yielding the desired product as brown oil (2.86 g, 7.2 mmol, 92%). ^{1}H NMR (200 MHz, C_6D_6): δ = 7.57 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Ar-*H*), 6.79 (d, $^4J_{H,H}$ = 2.4 Hz, 2 H, Ar-*H*), 3.23 (s, 2 H, ArC*H*$_2$N), 3.01 (t, $^3J_{H,H}$ = 5.1 Hz, 4 H, NC*H*$_2$C*H*$_2$O), 2.94 (s, 6 H, OC*H*$_3$), 2.34 (t, $^3J_{H,H}$ = 5.4 Hz, 4 H, NC*H*$_2$C*H*$_2$O) ppm. ^{13}C NMR (100.58 MHz, $CDCl_3$, 300 K): δ = 154.4 (*C*O), 134.1 (*C*H), 130.4 (*C*H), 125.3 (*C*), 111.1 (*C*), 110.5 (*C*), 70.4 (*C*H$_2$), 59.2 (O*C*H$_3$), 58.4 (*C*H$_2$), 53.6 (*C*H$_2$) ppm.

Synthesis of 1: Lig^{1}H (86 mg, 0.25 mmol) was dissolved in ether (1 mL) and cooled to –35 °C. While cold, it was added slowly to a pre-cooled solution of $ZnEt_2$ in hexane (1.0 M, 0.25 mL). The resulting bright yellow solution was warmed to room temp. and stirred for 1 h. The solvent was removed under reduced pressure, the resulting bright yellow solid was dissolved in pentane and the solution was left at –35 °C overnight. Colorless crystals of X-ray quality were separated from the solution, washed with cold pentane and dried under reduced pressure to afford **1** (91 mg, 0.20 mmol, 80%). $C_{23}H_{41}NO_3Zn$ (444.97): calcd. C 62.08, H 9.29, N 3.15; found: C 61.85, H 9.31, N 3.25. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 7.58 (d, $^4J_{H,H}$ = 2.7 Hz, 2 H, Ar-*H*), 6.88 (d, $^4J_{H,H}$ = 2.7 Hz, 2 H, Ar-*H*), 3.31 (s, 2 H, PhC*H*$_2$N), 2.96 (ddd, $^2J_{H,H}$ = 10.1, $^3J_{H,H}$ = 9.0, $^3J_{H,H}$ = 3.7 Hz, 2 H, NCH$_2$C*H*$_2$O), 2.85 (s, 6 H, OC*H*$_3$), 2.81 (dt, $^2J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.5 Hz, 2 H, NCH$_2$C*H*$_2$O), 2.41 (ddd, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 8.9, $^3J_{H,H}$ = 4.5 Hz, 2 H, NC*H*$_2$CH$_2$O), 2.17 (dt, $^2J_{H,H}$ = 13.3, $^3J_{H,H}$ = 4.0 Hz, 2 H, NC*H*$_2$CH$_2$O), 1.86 [s, 9 H, C(C*H*$_3$)$_3$], 1.63 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 1.46 [s, 9 H, C(C*H*$_3$)$_3$], 0.59 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{13}C NMR (100.58 MHz, C_6D_6, 298 K): δ = 164.4 (*C*O), 138.5 (*C*), 135.1 (*C*), 125.3 (*C*H), 124.1 (*C*H), 122.4 (*C*), 68.5 (*C*H$_2$), 59.6 (*C*H$_2$), 58.7 (O*C*H$_3$), 56.5 (*C*H$_2$), 35.9 [*C*(CH$_3$)$_3$], 34.2 [*C*(CH$_3$)$_3$], 32.4 [C(*C*H$_3$)$_3$], 30.2 [C(*C*H$_3$)$_3$], 13.5 (Zn-CH$_2$*C*H$_3$), –1.8 (Zn-*C*H$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C_7D_8, 301 K, selected resonances): δ = 3.30 (s, 2 H, PhC*H*$_2$N), 3.01 (ddd, $^2J_{H,H}$ = 10.0, $^3J_{H,H}$ = 9.0, $^3J_{H,H}$ = 3.7 Hz, 2 H, NCH$_2$C*H*$_2$O), 2.90 (s, 6 H, OC*H*$_3$), 2.81 (dt, $^2J_{H,H}$ = 10.1, $^3J_{H,H}$ = 4.5 Hz, 2 H, NCH$_2$C*H*$_2$O), 2.45 2.41 (ddd, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 9.0, $^3J_{H,H}$ = 4.5 Hz, 2 H, NC*H*$_2$CH$_2$O), 2.21 (dt, $^2J_{H,H}$ = 13.4, $^3J_{H,H}$ = 4.2 Hz, 2 H, NC*H*$_2$CH$_2$O), 1.56 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.49 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C$_7$D$_8$, 210 K, selected resonances): δ = ca. 3.1 (br. s, 2 H, PhC*H*$_2$N), 2.89 (br. s, 2 H, NCH$_2$C*H*$_2$O), 2.84 (s, 6 H, OC*H*$_3$), 2.60 (br. s, 2 H, NCH$_2$C*H*$_2$O), 2.29 (br. s, 2 H, NC*H*$_2$CH$_2$O), 1.87 (br. s, 2 H, NC*H*$_2$CH$_2$O), 1.76 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.69 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm.

Synthesis of 2: Lig^{2}H (165 mg, 0.62 mmol) was dissolved in ether (2 mL), cooled to –35 °C, and added slowly to a pre-cooled solution of ZnEt$_2$ in hexane (1.0 M, 0.63 mL). The resulting bright yellow solution was warmed to room temp. and stirred for 1 h. The solvent was removed under reduced pressure, the resulting bright yellow solid was dissolved in diethyl ether (ca. 3 mL overall) and the solution was left at –35 °C for 2 days. Colorless crystals of X-ray quality were separated from the solution, washed with cold ether and dried under reduced pressure to afford **2** (157 mg, 0.44 mmol, 71%). C$_{34}$H$_{58}$N$_2$O$_6$Zn$_2$ (721.61): calcd. C 56.59, H 8.10, N 3.88; found C 56.27, H 8.25, 3.86. ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 7.05 (d, $^4J_{H,H}$ = 1.9 Hz, 2 H, Ar-*H*), 6.66 (d, $^4J_{H,H}$ = 2.1 Hz, 2 H, Ar-*H*), 3.83 (s, 2 H, PhC*H*$_2$N), 3.13 (br. s, 4 H, NCH$_2$C*H*$_2$O), 2.86 (s, 6 H, OC*H*$_3$), 2.85 (br. s, 4 H, NC*H*$_2$CH$_2$O), 2.51 (s, 3 H, Ar-C*H*$_3$), 2.29 (s, 3 H, Ar-C*H*$_3$), 1.11 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.40 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C$_7$D$_8$, 301 K, selected resonances): δ = 3.65 (s, 2 H, PhC*H*$_2$N), 3.07 (br. s, 4 H, NCH$_2$C*H*$_2$O), 2.90 (s, 6 H, OC*H*$_3$), 2.61 (br. s, 4 H, NCH$_2$C*H*$_2$O), 2.47 (s, 3 H, Ar-C*H*$_3$), 2.29 (s, 3 H, Ar-C*H*$_3$), 1.51 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.38 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C$_7$D$_8$, 210 K, selected resonances): δ = 2.85 (s, 3 H, OC*H*$_3$), 2.77 (s, 3 H, OC*H*$_3$), 1.79 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.40 (br. s, 1 H, Zn-C*H*HCH$_3$), 0.31(br. s, 1 H, Zn-CH*H*CH$_3$) ppm. ^{13}C NMR (100.58 MHz, C$_6$D$_6$, 300 K): δ = 161.4 (*C*O), 132.4 (*C*H), 129.5 (*C*H), 128.4 (*C*), 124.1 (*C*), 123.4 (*C*), 68.9 (*C*H$_2$), 59.3 (*C*H$_2$), 58.4 (O*C*H$_3$), 53.2 (*C*H$_2$), 20.8 (Ar-*C*H$_3$), 17.8 (Ar-*C*H$_3$), 13.7 (Zn-CH$_2$*C*H$_3$), –1.7 (Zn-*C*H$_2$CH$_3$) ppm.

Synthesis of 3: Lig^{3}H (51 mg, 0.13 mmol) was dissolved in an ether/THF mixture (5 mL) and added to a solution of ZnEt$_2$ in hexane (1.0 M, 0.13 mL). The resulting dark yellow solution was stirred for 1.5 h. The solvent was removed under reduced pressure, and the resulting yellow solid was washed with pentane (ca. 2 mL) and ether (2 mL) and dried under reduced pressure to afford **3** (47 mg, 74%). X-ray quality crystals were obtained upon recrystallization from ether. C$_{30}$H$_{46}$Br$_4$N$_2$O$_6$Zn$_2$ (981.09): calcd. C 66.07, H 10.52, N 7.97; found C 66.11, H 10.77, N 7.88. ^{1}H NMR (400 MHz, C$_6$D$_6$, 300 K): δ = 7.82 (d, $^4J_{H,H}$ = 2.6 Hz, 2 H, Ar-*H*), 6.86 (d, $^4J_{H,H}$ = 2.6 Hz, 2 H, Ar-*H*), 3.06 (s, 2 H, PhC*H*$_2$N), 2.80 (s, 6 H, OC*H*$_3$), 2.69 (t, $^3J_{H,H}$ = 5.4 Hz, 4 H, NCH$_2$C*H*$_2$O), 2.24 (br. s, 2 H, NC*H*$_2$CH$_2$O), 1.99 (br. s, 2 H, NC*H*$_2$CH$_2$O), 1.53 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.49 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C$_7$D$_8$, 301 K, selected resonances): δ = 3.10 (s, 2 H, PhC*H*$_2$N), 2.85 (s, 6 H, OC*H*$_3$), 2.76 (t, $^3J_{H,H}$ = 5.4 Hz, 4 H, NCH$_2$C*H*$_2$O), ca. 2.3 (br. s, 2 H, NC*H*$_2$CH$_2$O), ca. 2.1 (br. s, 2 H, NC*H*$_2$CH$_2$O), 1.48 (t, $^3J_{H,H}$ = 8.1 Hz, 3 H, Zn-CH$_2$C*H*$_3$), 0.42 (q, $^3J_{H,H}$ = 8.1 Hz, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{1}H NMR (400 MHz, C$_7$D$_8$, 200 K, selected resonances): δ = around 2.8 (broad and flat resonance, 14 H), 2.26 (br. s, 2 H), 1.78 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, Zn-CH$_2$C*H*$_3$), ca. 0.45 (br. s, 2 H, Zn-C*H*$_2$CH$_3$) ppm. ^{13}C NMR (50.29 MHz, C$_6$D$_6$, 298 K): δ = 135.6 (*C*H), 132.1 (*C*H), 128.4 (*C*), 126.2 (*C*), 117.1 (*C*), 67.9 (*C*H$_2$), 58.5 (O*C*H$_3$), 57.9 (*C*H$_2$), 56.1 (*C*H$_2$), 13.4 (Zn-CH$_2$*C*H$_3$), –1.8 (Zn-*C*H$_2$CH$_3$) ppm.

Supporting Information (see footnote on the first page of this article) includes VT NMR spectra for complexes **1**–**3**.

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