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Formation of Unusual Trinuclear Assemblies: Scope and Mechanism of Zn(salphen)-Templated Activation of Pyridine-Alcohol Substrates

Marta Martínez Belmonte,[a] Eduardo C. Escudero-Adán,[a] Jordi Benet-Buchholz,[a] and Arjan W. Kleij*[a,b]

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We report here a full study on the templating properties of a series of Zn(salphen) complexes toward pyridine-alcohol substrates by selective activation of the OH group providing trinuclear supramolecular assemblies as products. The templated process was investigated by various techniques including NMR spectroscopy, MALDI-TOF mass spectrometry and X-ray diffraction studies. A range of substrates were tested to reveal the scope and limitations of this process. The successful examples furnish remarkable trinuclear supramolecular assemblies comprising a non-symmetrical central unit made up of two monodeprotonated pyridine-alcohol ligands that coordinate a Zn^{II} ion. The anionic oxygen atoms of this central Zn complex in turn are both associated with a Zn(salphen) unit. A number of model compounds were also prepared and substantiated the view that the first step in the templated mechanism involves the coordination of the alcohol function to the Zn^{II} centre of the salphen complex. Hereafter, a double proton transfer to the salphen ligand occurs with simultaneous formation of the nonsymmetrical central complex, which combines with two Zn(salphen) modules through coordinative Zn–O bonds. The latter may be regarded as effective supramolecular protecting groups: stability studies performed in more polar media have revealed the full reversibility of the templated process. The reactivity of the Zn(salphen) complex towards alcoholic substrates may be useful in Lewis acid mediated synthesis.

Introduction

Nature uses templated synthesis as a tool to selectively produce molecules of biological importance. The key aspect within these processes is the increase in the effective molarity of the reaction components by a macromolecular template that directs the chemical reactivity even at extremely low concentrations.[1] In the context of chemical synthesis such template events are usually undertaken at much higher (mM) concentrations for various targeted structures with high molecular complexity.[2] For instance, Leigh and co-workers reported on the first example of an "active metal template reaction" to yield a [2]rotaxane[3] using a highly effective and mild copper(I)-catalyzed terminal alkyne-azide 1,3-cycloaddition (CuAAC).[4] In this approach, a macrocycle is used, which can bind the metal ion endotopically within its cavity. The complexed metal ion is subsequently able to promote covalent bond formation between two suitable "half-thread" units. After the templated rotaxane synthesis, the metal ion may be depleted from the [2]rotaxane structure. By using a similar CuAAC reaction, also a bis(triazole) molecular shuttle could be constructed, and the metal-dependent shuttle dynamics were linked with new sensing potential.[5]

Metal templation[6] as a means towards the selective synthesis of complicated structures is a rather recent phenomenon in the field of salen chemistry,[7] but yet has demonstrated its usefulness for the synthesis of functional inorganic,[8] supramolecular[9] and catalytic materials.[10] On the other hand, metal templation has also proven to be a successful strategy in the preparation of various nonsymmetrical (multi)salen complexes.[11]

We recently discovered that Zn^{II}(salphen) complex **1** (salphen = *N*,*N*′-disalicylidene-1,2-phenylenediamine) is able to template the synthesis of the nonsymmetrical Zn^{II} complex **A** (Figure 1) by heating 2,6-pyridinedimethanol (dmpy) in the presence of (excess) **1**.[12] The resulting complex, an unusual dideprotonated $(dmpy)_2Zn$ derivative, was stabilized by two Zn(salphen) complexes through coordinative Zn–O_{dmpy} bond patterns. In view of the increasing importance of templating effects brought about by (salen) metal structures and in particular directed by Zn-centred complexes,[6] the mechanistic features of this template effect and the scope of the process are important aspects to expose. Obviously, such information is valuable in understanding the potential of the Zn[sal(ph)en] family of structures as homogeneous catalysts[13] for Lewis acid mediated

[a] Institució Catalana de Recerca i Estudis Avançats (ICREA)
Lluis Companys 23, 08010 Barcelona, Spain
[b] Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona, Spain
Fax: +34-977-920-224
E-mail: akleij@iciq.es
http://www.iciq.es
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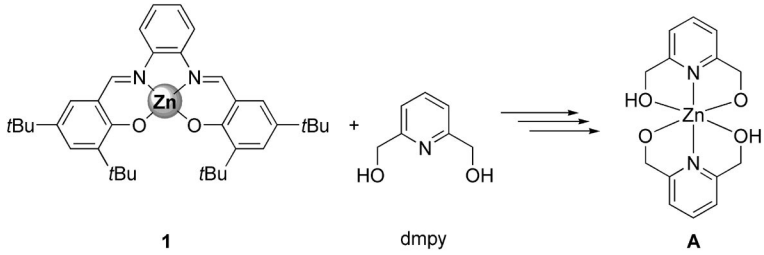


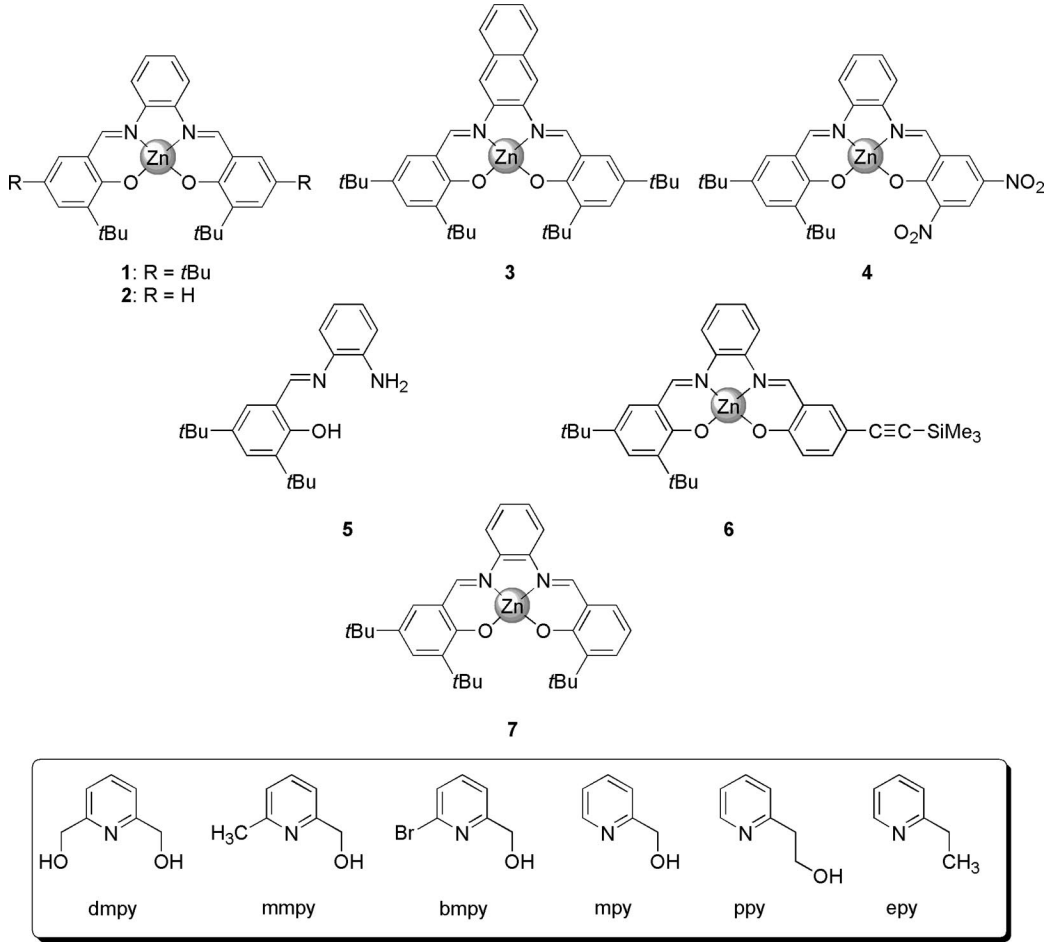
Figure 1. Formation of nonsymmetrical Zn complex **A** by templated synthesis starting from **1** and 2,6-pyridinedimethanol.

conversions.[14] Here we report details of an extensive study that links the templating properties of various Zn(salphen) complexes in the presence of pyridine-alcohol substrates, and we will present evidence for the proposed mode of action that has led to a small library of unexpected supramolecular Zn_3 structures.

Results and Discussion

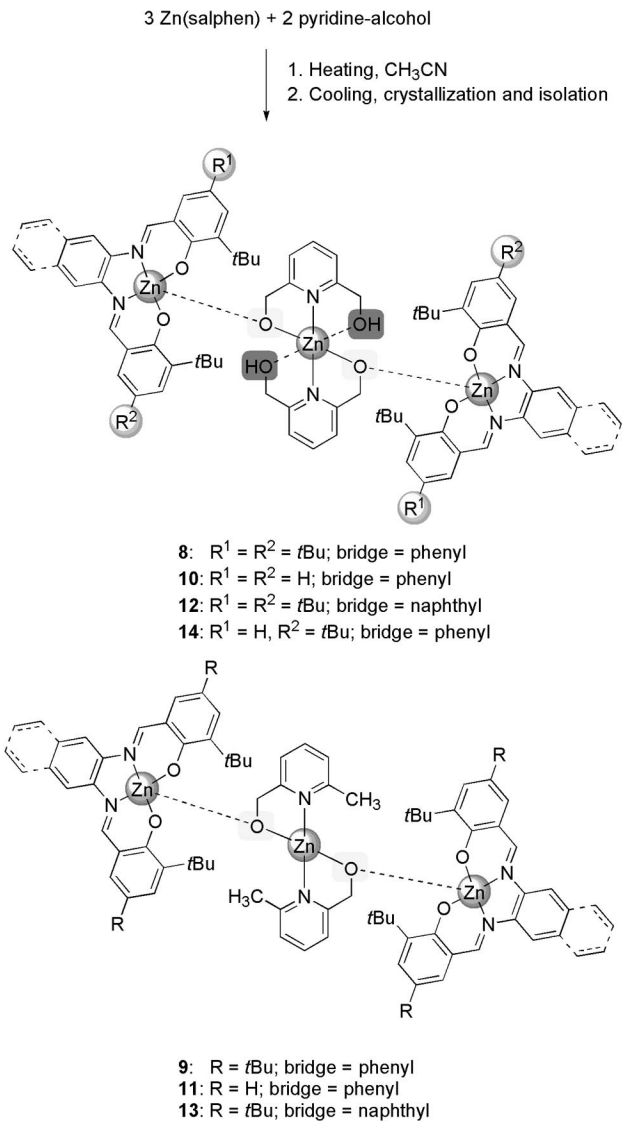
Synthesis of Assemblies

Initially, Zn(salphen) complex **1** was combined with pyridine-alcohol ligand dmpy (Scheme 1) to investigate its coordination features. Heating of a mixture containing **1** and excess dmpy afforded, after cooling, crystalline material that was characterized by X-ray diffraction (XRD) as an unexpected trinuclear Zn_3 assembly **8** (Scheme 2).[12] The formation of the Zn_3 assembly is accompanied by the release of 1 equiv. of salphen-H_2, i.e. demetalated **1**. The reaction was therefore repeated with a 3:2 combination of **1** and dmpy, and this afforded the Zn_3 assembly **8** (Scheme 2) in 40% isolated yield as a yellow crystalline solid. It should be noted that heating to reflux temperature of the mixture only takes place for a short period of time (10–20 s), after which the trinuclear complex crystallizes from solution upon cooling. Simple filtration or decan-



Scheme 1. Structures of Zn(salphen) complexes **1**–**4** and **6**–**7**, monoimine reagent **5** and the substrates/ligands for the templated synthesis and reference studies.

tation then affords pure materials depending on the time of crystallization and whether fractionated crystallization is applied.



Scheme 2. General procedure for the formation of trinuclear Zn_3 assemblies **8**–**14** by Zn(salphen) templation.

A similar methodology was then applied to various combinations of Zn(salphen) complexes **1**–**4** and **6**–**7**, and pyridine-alcohol ligands (Scheme 1) to afford trinuclear Zn_3 assemblies **9**–**14** in moderate isolated yields [40–61%, except for **9** (19%)] also as (micro)crystalline materials. A further increase in isolated yield of the pure compounds was hampered by the co-crystallization of the respective salphen ligand that is released in the templated process (vide infra). In order to assess the reproducibility of the procedure, some of the reactions were performed in duplicate and showed consistent behaviour in terms of isolated yield and purity of the Zn_3 assemblies.

Of particular note is the lack of reactivity found when Zn(salphen) complexes **4** and **6** were used. Heating of either of these complexes in the presence of mmpy or dmpy did not afford any crystalline product, and inspection of the solution components by ^{1}H NMR spectroscopy showed only the presence of the starting materials. It is well known that complexes such as **4** and **6** form dimers both in the solid state and in solution, and this limits the ability of these complexes in the templation event (vide infra).

X-ray Diffraction Studies

The solid-state features of trinuclear species **9**, **10**, **12** and **14** were investigated by X-ray diffraction (XRD). The molecular structures for these assemblies are shown in Figure 2A–D. Selected bond lengths/angles are summarized in Table 1.[15]

In the structure based on mmpy (i.e., **9**), the central $Zn(mmpy)_2$ complex comprises a Zn ion with a distorted tetrahedral geometry. Both Zn–O and both Zn–N bond lengths around Zn(2B) are similar, whereas the angles deviate substantially from ideal tetrahedral angles (Table 1). A probable cause of this significant disruption of an ideal tetrahedral geometry is the interaction of both anionic O(3B) and O(4B) with the two Zn(salphen) complexes through O–Zn coordination. This is also reflected by the bond lengths/angles within the Zn(salphen) complexes. For instance, Zn(1B) in one of the salphen complexes is nonsymmetrically positioned within the N_2O_2 donor set and significantly tilted from this coordination plane due to the strong interaction between Zn(1B) and anionic O(3B).

The dmpy-based Zn_3 assemblies **10**, **12** and **14** show similar features for the coordinated Zn(salphen) units. However, the differences between the Zn–O and Zn–N bond lengths within the coordination geometry around the metal ion (Table 1) are generally larger, accompanied by a much shorter Zn–O_{dmpy} distance [1.975(2)–1.995(3) Å] as compared to the Zn–O_{dmpy} distance [Zn(1B)–O(3B) 2.020(2) Å; Zn(3B)–O(4B) 2.014(2) Å] in **9**. For the dmpy-containing assemblies the central complex shows a number of interesting features. Each dmpy ligand is bonded to the Zn ion in a tridentate *O*,*N*,*O*-chelating fashion with two considerably different Zn–O distances. For example, in **10** the bond lengths Zn(1)–O(3) and Zn(1)–O(4) are 1.970(2) and 2.542(2), respectively. For the other Zn(dmpy) fragment in **10** and $Zn(dmpy)_2$ units in **12** and **14** comparable bond length characteristics are found. This large difference in bond length can only be rationalized by considering the presence of both a neutral and an anionic oxygen atom in each dmpy ligand. The distance between the anionic oxygen donors and the Zn ion in the central unit is comparable with the bond lengths found for the Zn–O motifs within the Zn(salphen) units. The other Zn–O_{dmpy} interaction is weak in nature and can be explained by the presence of an OH donor fragment. Upon coordination, it completes a highly distorted octahedral surrounding of the central Zn ion. In structures **10**, **12** and **14** this distortion is reflected by several bond angles, and the N–Zn–N serves as the most prominent one. The N–Zn–N angles in **10** [N(3)–Zn(1)–N(4) 138.88(9)°], **12** [N(1)–Zn(3)–N(2) 141.16(9)°] and **14** [N(3)–

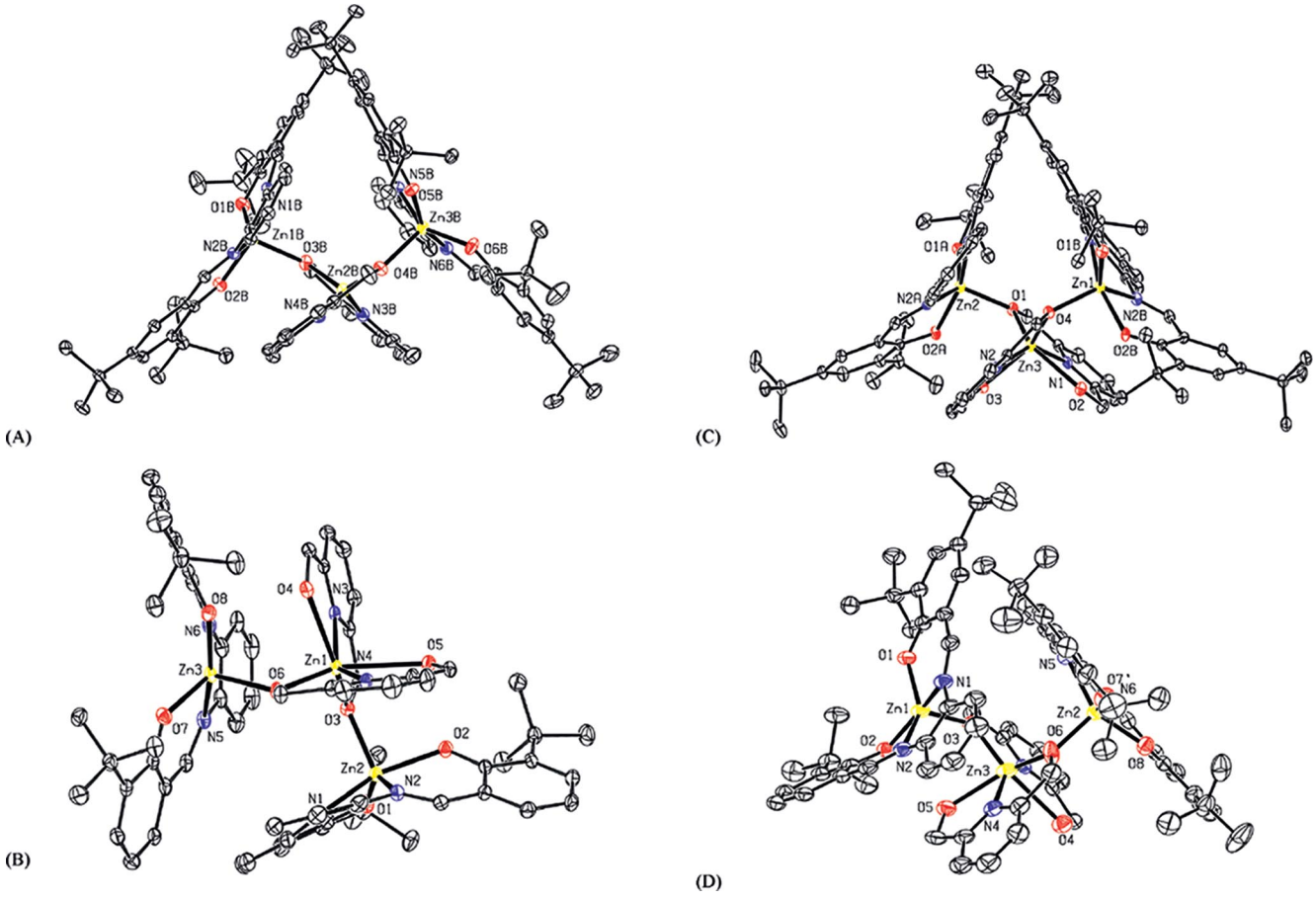


Figure 2. Molecular structures for Zn_3 assemblies **9** (A), **10** (B), **12** (C) and **14** (D). Cocrystallized solvent molecules and hydrogen atoms are omitted for clarity, and only a partial numbering scheme is given. Thermal ellipsoids are shown at the 50% probability level. For **9**, only one of the three independent molecules in the unit cell is shown.

Table 1. Listing of selected bond lengths [Å] for assemblies **9**, **10**, **12** and **14** with esds in parentheses.[a]

Complex **9**				Complex **12**			
Zn(2B)–O(3B)	1.933(2)	O(3B)–Zn(2B)–O(4B)	128.95(8)	Zn(1)–O(1B)	1.963(2)	O(1B)–Zn(1)–O(2B)	100.96(8)
Zn(2B)–O(4B)	1.924(2)	N(3B)–Zn(2B)–N(4B)	128.89(8)	Zn(1)–O(2B)	2.037(2)	N(1B)–Zn(1)–N(2B)	77.22(9)
Zn(2B)–N(3B)	2.023(2)	O(3B)–Zn(2B)–N(3B)	85.26(8)	Zn(1)–O(4)	1.975(2)	O(1B)–Zn(1)–N(2B)	134.25(8)
Zn(2B)–N(4B)	2.025(2)	O(4B)–Zn(2B)–N(4B)	85.40(8)	Zn(1)–N(1B)	2.084(2)	O(2B)–Zn(1)–N(1B)	159.53(8)
Zn(1B)–O(1B)	1.980(2)	O(3B)–Zn(2B)–N(4B)	112.97(8)	Zn(1)–N(2B)	2.116(2)	O(2B)–Zn(1)–O(4)	91.54(7)
Zn(1B)–O(2B)	2.002(2)	O(4B)–Zn(2B)–N(3B)	120.65(8)	Zn(3)–O(1)	1.969(2)	N(1)–Zn(3)–N(2)	141.16(9)
Zn(1B)–O(3B)	2.020(2)	N(1B)–Zn(1B)–O(2B)	158.70(7)	Zn(3)–O(2)	2.496(2)	O(1)–Zn(3)–O(2)	151.44(7)
Zn(1B)–N(1B)	2.104(2)	N(2B)–Zn(1B)–O(1B)	143.97(8)	Zn(3)–O(3)	2.442(2)	O(3)–Zn(3)–O(4)	152.05(7)
Zn(1B)–N(2B)	2.090(2)	O(1B)–Zn(1B)–O(2B)	96.06(7)	Zn(3)–O(4)	1.991(2)	O(2)–Zn(3)–O(3)	106.54(7)
Zn(3B)–O(4B)	2.014(2)	N(1B)–Zn(1B)–N(2B)	77.28(7)	Zn(3)–N(1)	2.044(2)	O(1)–Zn(3)–O(4)	104.63(8)
Zn(3B)–O(6B)	1.975(2)	O(1B)–Zn(1B)–O(3B)	103.12(7)	Zn(3)–N(2)	2.031(2)	O(2)–Zn(3)–N(1)	70.78(8)
Complex **10**				Complex **14**			
Zn(2)–O(1)	1.967(2)	O(1)–Zn(2)–O(2)	101.40(9)	Zn(2)–O(7)	2.012(7)	O(7)–Zn(2)–O(8)	85.8(2)
Zn(2)–O(2)	2.054(2)	N(1)–Zn(2)–N(2)	76.51(9)	Zn(2)–O(8)	1.994(2)	N(5)–Zn(2)–N(6)	77.46(9)
Zn(2)–O(3)	1.979(2)	O(1)–Zn(2)–N(2)	140.60(9)	Zn(2)–O(6)	1.995(3)	O(7)–Zn(2)–N(6)	137.1(3)
Zn(2)–N(1)	2.115(2)	O(2)–Zn(2)–N(1)	157.97(9)	Zn(2)–N(5)	2.096(2)	O(8)–Zn(2)–N(5)	149.9(1)
Zn(2)–N(2)	2.114(2)	O(1)–Zn(2)–O(3)	106.52(8)	Zn(2)–N(6)	2.128(2)	O(6)–Zn(2)–O(8)	103.2(1)
Zn(1)–O(3)	1.970(2)	N(3)–Zn(1)–N(4)	138.88(9)	Zn(3)–O(3)	1.969(2)	N(3)–Zn(3)–N(4)	145.7(1)
Zn(1)–O(4)	2.542(2)	O(3)–Zn(1)–O(4)	151.92(8)	Zn(3)–O(4)	2.587(2)	O(5)–Zn(3)–O(6)	155.31(9)
Zn(1)–O(5)	2.571(2)	O(5)–Zn(1)–O(6)	150.80(8)	Zn(3)–O(5)	2.440(3)	O(3)–Zn(3)–O(4)	154.92(8)
Zn(1)–O(6)	1.977(2)	O(4)–Zn(1)–N(3)	70.79(8)	Zn(3)–O(6)	2.001(3)	O(3)–Zn(3)–O(6)	109.8(1)
Zn(1)–N(3)	2.045(2)	O(5)–Zn(1)–N(4)	70.57(8)	Zn(3)–N(3)	2.028(2)	O(4)–Zn(3)–O(5)	100.09(8)
Zn(1)–N(4)	2.044(2)	O(3)–Zn(1)–O(6)	107.44(8)	Zn(3)–N(4)	2.028(3)	N(4)–Zn(3)–O(6)	82.7(1)

[a] For simplicity only a full set of bond lengths within one Zn(salphen) module of each structure is presented.

Zn(3)–N(4) 145.7(1)°] are far from ideal but are likely dictated by both the presence of two different oxygen donors in each dmpy ligand as well as the coordinative $Zn–O_{dmpy}$ patterns between the central unit and the Zn(salphen) complexes.

Each trinuclear assembly can be regarded as an unusual nonsymmetrical $Zn(dmpy)_2$ complex[16] shielded by two supramolecular Zn(salphen) groups. Although in the solid state these species are completely stable, in solution the assembly process can be reversed (weakening of the coordinative $Zn–O_{dmpy}$ interaction) by an increase in the polarity of the medium (vide infra).

NMR Spectroscopic Analysis

The Zn_3 assemblies were also examined by NMR spectroscopy, and one of both series (those based on dmpy and mmpy, Scheme 2) will serve as illustrative examples for the other Zn_3 structures.

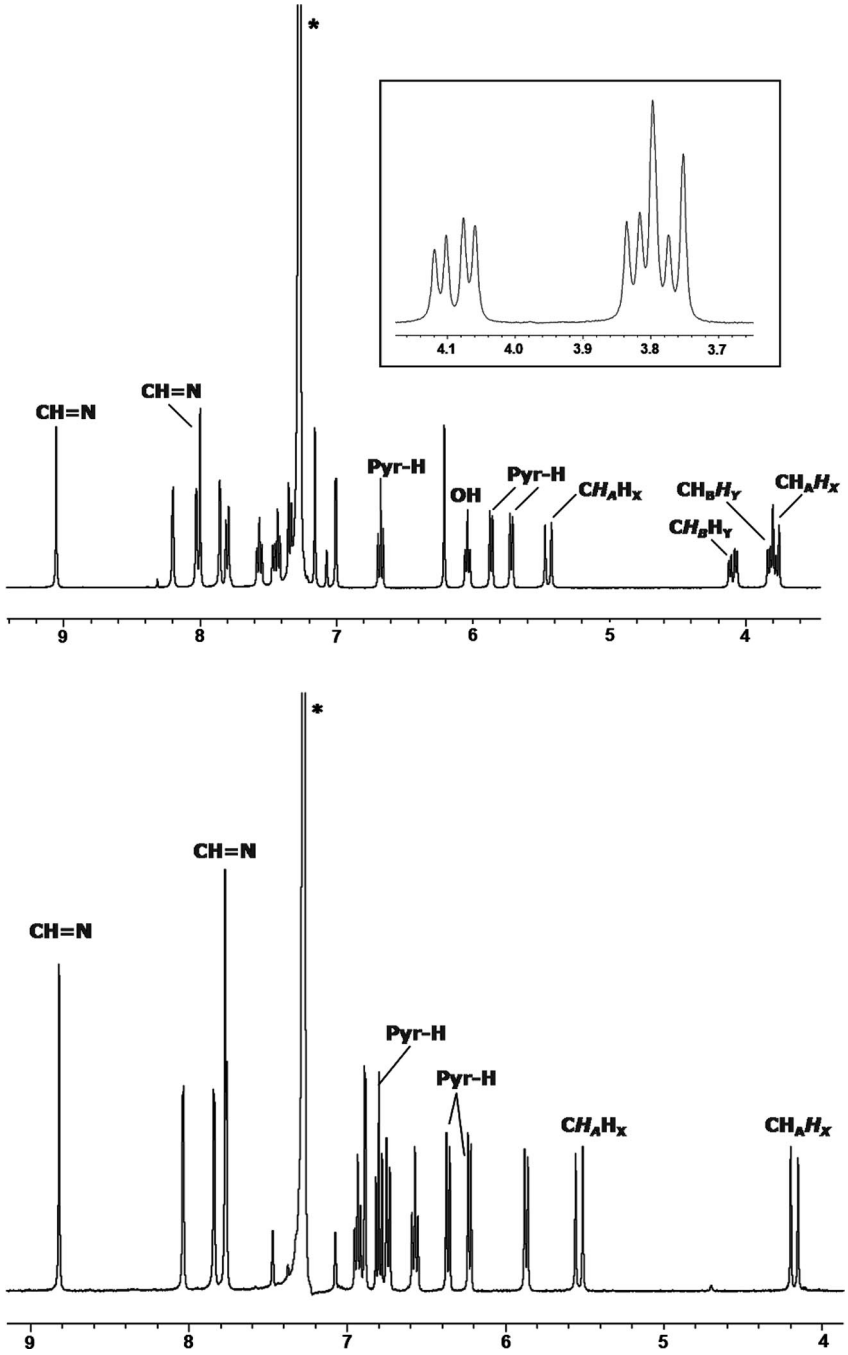


Figure 3. Part of the ^1H NMR spectrum ([D_6]benzene, top) of trinuclear assembly **12** and partial assignment. The asterisk denotes the solvent residual peak. The inset shows part of the methylene region at $\delta \approx 4$ ppm, the bottom a part of the ^1H NMR spectrum ([D_6]-benzene) of Zn_3 assembly **9**.

All measurements were carried out in a noncoordinating solvent ([D_6]benzene), an aspect that proved to be essential for the stability of the trinuclear assemblies. For **12** the region δ = 4–9 ppm is presented in Figure 3. The coordination of the Zn(salphen) complexes under these conditions is evident since all the salphen protons are magnetically nonequivalent. For instance, the imine protons give rise to two separate signals at δ = 9.05 and 8.00 ppm. The reason for the large separation of both signals is the close proximity of one of these imine hydrogen atoms to aromatic groups of the assembly causing a magnetic anisotropy. In the $^{13}C\{^1H\}$ NMR spectrum of **12** signals of two imine carbon atoms are observed, consistent with the nonsymmetrical surrounding of the Zn(salphen) complex. The *t*Bu groups of the Zn(salphen) unit give rise to four distinct resonances (both in the ^1H and $^{13}C\{^1H\}$ NMR spectra), further supporting the binding to the central Zn(dmpy)$_2$ complex. The presence of a nonsymmetrical central Zn complex is clearly demonstrated by the occurrence of two separate AX patterns ($^2J \approx 17$–18 Hz) of which only one shows a hyperfine coupling with the OH group, which in turn is present as a triplet at δ = 6.04 ppm. Three pyridine resonances are further testament of the nonsymmetrical nature of the central unit.

For the assemblies based on mmpy (Scheme 1) similar observations were made (Figure 3, bottom), i.e. all salphen and pyridine protons are observed as separate signals, and one clear AX pattern is noted for the methylene fragment. Combined with the absence of an OH resonance, the NMR features support the stability of the mmpy-based Zn_3 assemblies in solution.

The NMR characterization of crystalline **14** gave highly complicated spectra, which are difficult to assign (Supporting Information). Although generally the ^1H NMR ([D_6]-benzene) of **14** shows large resemblance with those measured for trinuclear species **8**–**13**, the multiple patterns are evidently not of a single species. Although in the solid state (see Figure 2D) only one type of assembly is observed, we believe that in solution two types of isomeric assemblies are present. The clearest region (i.e., aliphatic; Supporting Information) shows 9 distinct peaks for the *t*Bu groups. NMR spectroscopy additionally revealed that the involved species do not interconvert at room temperature during at least 24 h, and thus the involved isomers are stereochemically stable. Considering the hindered rotation around the Zn(salphen)–O_{dmpy} coordinative bond brought about by the large *t*Bu groups of the salphen ligand, once this (strong) Zn–O bond is formed[17] the conformation of the assembly is locked. The presence of the nonsymmetrical complex **7** within the assembly and the two positions it can take with respect to the central Zn(dmpy)$_2$ unit can provide two isomeric forms of **14** where both units **7** have their di-*tert*-butylated aryl groups in a *syn* (cf., X-ray data of **14**; Figure 2D) or *anti* orientation (Figure 4).

Based on symmetry considerations with the aid of molecular models, the *syn* isomer should give rise to three distinct *t*Bu resonances, whereas the *anti* isomer would afford six *t*Bu peaks. This is in line with the observation of signals of a total of 9 *t*Bu groups in the ^1H NMR spectrum of **14**. The ratio between both isomeric forms could be deduced from signal integration and is close to 1.

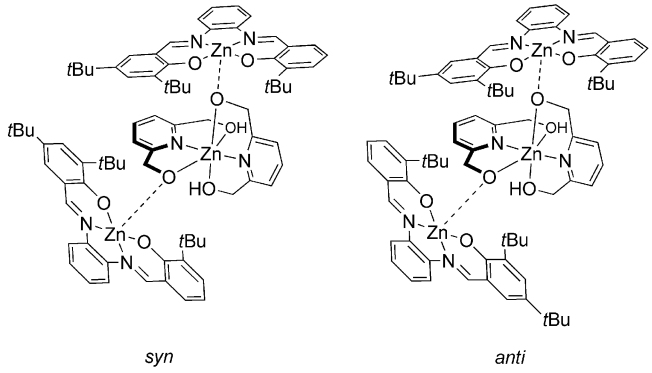


Figure 4. Schematic representation of the *syn* and *anti* isomers of complex **14**.

Mass Spectrometric Studies

The mass spectrometric analysis of the trinuclear assemblies was carried out by MALDI-TOF (pyrene matrix). All assemblies gave similar results, i.e. a typical fragmentation was observed that includes the loss of one pyridine-alcohol ligand and one Zn(salphen) unit. For instance, for **11** fragment ions were observed at *m*/*z* = 679.3 (calcd. 679.2) and 678.3 (calcd. 678.2), which correspond to [M – mmpy – **2** + H]$^+$ and [M – mmpy – **2**]$^+$, respectively (Supporting Information). The Zn_2 clusters show typical isotopic patterns, which make the identification of these fragment ions straightforward. Although no direct observation of the molecular ions was accomplished, the presence of these substructural, dinuclear species is further indication for the existence and formation of the trinuclear assemblies.

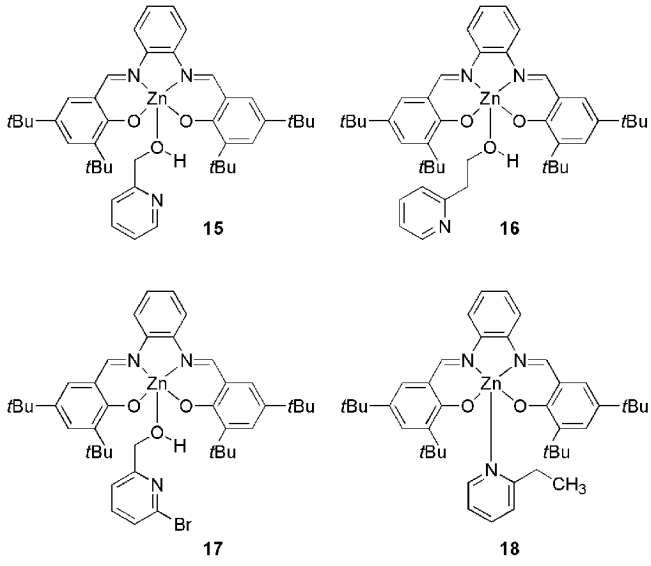
Templated Mechanism

A number of model compounds (Scheme 1) and spectroscopic variations were examined in order to reveal in more detail the operating mechanism leading to the Zn_3 assemblies. First of all, upon changing the polarity of the solvent, the equilibrium in the templated process may be shifted. This was demonstrated by ^1H NMR spectroscopy using different deuterated solvents. As mentioned earlier,[12] in [D_6]-benzene, the trinuclear assemblies are stable, but upon increasing the polarity by either cosolvation ([D_6]DMSO, 5–10%, v/v) or changing the solvent for [D_6]acetone the formation of the Zn_3 assembly may be partially or fully blocked, and the starting compounds [Zn(salphen) complex and pyridine-alcohol ligand] are obtained (Supporting Information). This infers that in these latter cases the (initial) interaction of the pyridine-alcohol with the Lewis acidic Zn centre in the salphen complex suffers by competition of sol-

vent molecules. A second important observation is the lack of templating reactivity in the presence of Zn(salphen) complexes **4** and **6**.

Both derivatives lack at one side of the N_2O_2 coordination pocket the presence of sufficient steric bulk needed to prevent the complex from dimerization through μ_2-O bridging. This dimerization phenomenon for Zn(salen) species has been well documented in the literature,[18] and formation of mononuclear species in solution can only be achieved by addition of (excess) appropriate, strongly donating ligands such as pyridines. The unreactive nature of both **4** and **6** in the presence of dmpy suggests that the initial stage of the templated process should involve coordination of the alcohol function to the Zn centre rather than ligation through the nitrogen donor atom. We therefore carried out several additional experiments that support this view.

First, the ^{1}H NMR spectra of 1:1 combinations of **1** and 2-pyridinemethanol or 2-(2-pyridine)ethanol (mpy and ppy, respectively, Scheme 1) were compared with free mpy and ppy. Remarkably, in the case of mpy ligation a significant upfield shift for the OH fragment signal was noted ($\Delta\delta$ = –0.12 ppm), whereas the pyridine *ortho*-proton signal virtually showed no displacement.[19] This effect was even more pronounced for the ppy coordination, and large upfield shifts were noted for both the OH ($\Delta\delta$ = –0.15 ppm) and the CH_2O fragment ($\Delta\delta$ = –0.26 ppm). The NMR spectroscopic data suggest a clear preference for oxygen atom ligation in the case of mpy and ppy. This was also supported by XRD studies of crystalline material obtained for both **1**·mpy (**15**, Scheme 3) and **1**·ppy (**16**, Scheme 3) of which the results are visualized in Figure 5.[20]



Scheme 3. Schematic structures for 1:1 coordination complexes **15**–**18**.

Other pyridine(-alcohol) ligands (Scheme 1; bmpy and epy) were then also investigated and their molecular structures determined by XRD. In the case of **1**·bmpy (**17**)[20,21] a 1:1 coordination complex as determined for **15** and **16** was characterized, whereas for epy the (expected) pyridine ligation was observed (**18**, Figure 5). The structure of **18** helps to rule out the option that the mpy, ppy and bmpy ligands are unable to coordinate through the N_{pyr} atom because of too much steric infringement. Since mpy, ppy and epy are of comparable size they should have very similar

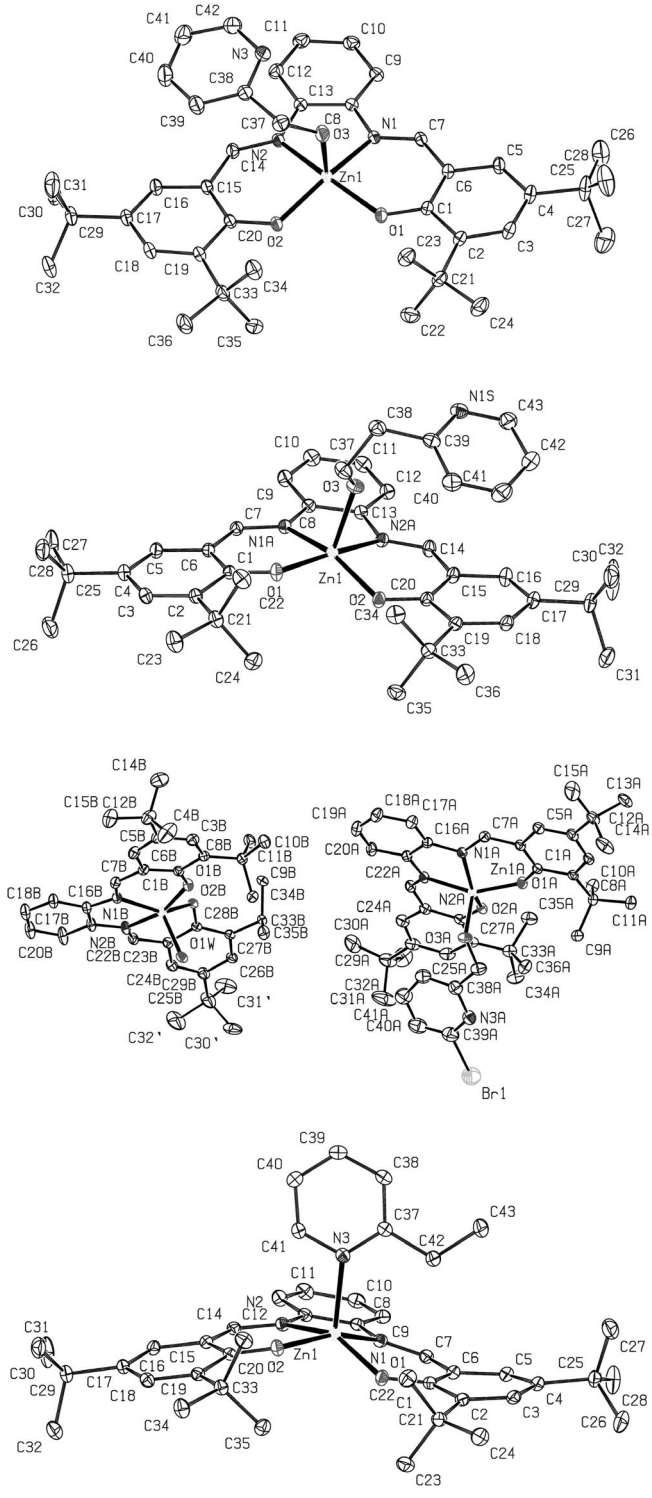
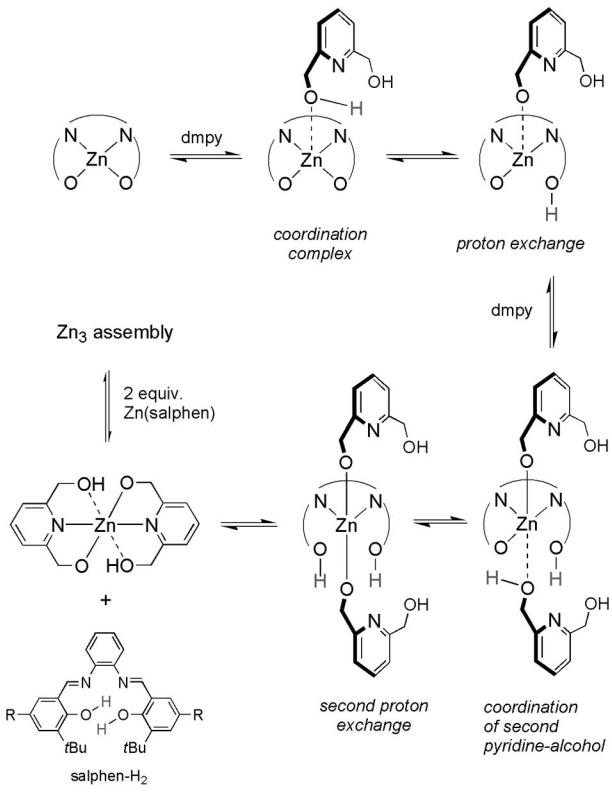


Figure 5. Molecular structures determined for **15**–**18** (from top to bottom). Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity.

steric features upon coordination to **1**; hence, the preference for oxygen atom coordination in the case of mpy and ppy is apparent.

The crystallographic and additional NMR spectroscopic results of these model compounds clearly show that the templated process that gives access to the Zn_3 assemblies is a function of the pyridine-alcohol structure, and that indeed the coordination of the alcohol unit can be considered the first step in the mechanism (Scheme 4). Another interesting observation is that only in the case of dmpy and mmpy as substrates, the coordination to the Zn(salphen) structure leads to trinuclear assembly formation (final product of templated process), whereas in the case of mpy, ppy and bmpy the initial 1:1 coordination complexes are isolated under comparable experimental (i.e, crystallization) conditions. At this stage, we believe that isolation of the crystalline 1:1 complexes in the case of mpy, ppy and bmpy is imparted by their superior crystallization properties as compared to their respective Zn_3 assemblies. Nonetheless, their isolation helps to support the proposed mechanistic pathway (Scheme 4). The observation of the diprotonated salphen ligands as by-products of the templated synthesis of the trinuclear assemblies (see Exp. Sect.) points to a double proton exchange between the coordinated pyridine-alcohol ligand and the phenolic position of the salphen ligand. It also shows that a proton acceptor is needed to accomplish trinuclear assembly formation and that the Zn(salphen) complex has a dual role in the templated event.



Scheme 4. Proposed templated mechanism for the formation of trinuclear assemblies **8**–**14**. Here, the mechanism is detailed for the dmpy-based assemblies.

Beside the double proton transfer, the Zn ion is transferred to the monoanionic pyridine-alcohol ligand (dmpy) and combines as $Zn(dmpy)_2$. In the final step (Scheme 4), supramolecular association of two Zn(salphen) complexes (those not involved in the template mechanism) occurs through $Zn–O_{dmpy}$ interactions. A relatively polar medium (acetone, DMSO) is able to reverse the template process completely, and this is a consequence of the highly competitive coordination features of these solvents with respect to pyridine-alcohol oxygen atom ligation: the starting point for the template-induced formation of these trinuclear assemblies.

Conclusions

This work has shown that Zn(salphen) complexes are excellent Lewis acid activators for oxygen atom containing substrates. As a representative case, we have studied in detail the activation of pyridine-alcohol derivatives and isolated both models for the initial stage of the templated process as well as final templated products (i.e., trinuclear Zn_3 assemblies). The isolation and full characterization of these supramolecular structures by solution and solid-state techniques, and the additional experiments and accompanying spectroscopic studies support the proposed mechanistic pathway that leads to these unusual assemblies. An initial coordination complex is formed (Zn–O interaction), and a subsequent single proton transfer from each pyridine-alcohol within the coordination sphere of the Zn(salphen) complex affords the central, nonsymmetrical unit of the Zn_3 assembly. Both anionic oxygen atoms of this unit then recombine in situ with 2 equiv. of Zn(salphen) to afford the trinuclear assembly. The Zn(salphen) complexes may be considered as supramolecular protecting groups, which under polar conditions (cf., NMR studies in $[D_6]$acetone and $[D_6]$DMSO) are decoordinated, and the templated process is then reversed. Our present findings illustrate that the substitution on the salphen ligand has a large impact on the reactivity. Whereas dimeric Zn(salphen) complexes do not show any observable reactivity towards the presented pyridine-alcohol ligands, mononuclear derivatives **1**–**3** and **7** (Scheme 1) easily generate the trinuclear assembly products. We are now investigating the catalytic potential of (chiral) Zn(salphen) derivatives towards various oxygen and nitrogen atom containing substrates.

Experimental Section

General Information: All reactions were performed in air by using commercial reagents and solvents without further purification. All pyridine-alcohol derivatives were purchased from commercial sources and used as such. Compounds **1**–**2**,[22] **3**,[11c] **4**,[23] **5** (Scheme 1),[24] **7**[25] and 5-(trimethylsilylethynyl)salicylaldehyde[26] were prepared as previously reported. Elemental analyses were performed at the Unidad de Análisis Elemental from the University of Santiago de Compostela (Spain). All NMR measurements were carried out with a Bruker 400 MHz spectrometer at ambient temperature unless stated otherwise, and chemicals shifts are given in ppm vs. tetramethylsilane. NMR assignments were in all cases sup-

ported by separate COSY and NOESY measurements. Mass spectrometric data were obtained from the Research Support unit of the ICIQ. X-ray diffraction studies were performed at the ICIQ facilities. CCDC-743222 to CCDC-743229 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.

Zn(salphen) Complex 6: To a solution of monoimine **5** (0.34 g, 1.05 mmol) in MeOH (25 mL) was added solid 5-(trimethylsilylethynyl)salicylaldehyde (0.23 g, 1.05 mmol) and then a solution of $Zn(OAc)_2{\cdot}2H_2O$ (0.29 g, 1.32 mmol) dissolved in MeOH (5 mL). The mixture was stirred for 3 h and then filtered to furnish the title compound as a yellow to orange solid. Yield 483.5 mg (0.822 mmol, 78%). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.00 (s, 1 H, CH=N), 8.97 (s, 1 H, CH=N), 7.90 (d, ^3J = 7.9, ^4J = 1.3 Hz, 1 H, ArH), 7.87 (d, ^3J = 7.9, ^4J = 1.2 Hz, 1 H, ArH), 7.56 (d, ^4J = 2.3 Hz, 1 H, ArH), 7.41–7.50 (m, 2 H, ArH), 7.39 (d, ^4J = 2.7 Hz, 1 H, ArH), 7.25 (d, ^3J = 8.8, ^4J = 2.3 Hz, 1 H, ArH), 7.16 (d, ^4J = 2.6 Hz, 1 H, ArH), 6.65 (d, ^3J = 8.8 Hz, 1 H, ArH), 1.44 [s, 9 H, C(CH$_3$)$_3$], 1.29 [s, 9 H, C(CH$_3$)$_3$], 0.21 [s, ^2J(Si-H) = 3.5 Hz, 9 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (10 MHz, [D$_6$]acetone + 5% [D$_5$]-pyrdine): δ = 174.03, 171.92, 164.55, 162.91, 141.94, 141.40, 140.90, 140.16, 137.29, 134.48, 130.13, 129.77, 128.29, 127.23, 124.78, 120.13, 118.97, 116.90, 107.32, 107.13, 90.30, 35.83, 34.05, 31.42, 29.75, 0.41 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 586 [M$^+$] (calcd. 586.2), 571 [M – CH$_3$]$^+$ (calcd. 571.2). $C_{33}H_{38}N_2O_2$-SiZn (588.16): calcd. C 67.39, H 6.51, N 4.76; found C 67.25, H 6.42, N 4.87.

Trinuclear Assembly Zn(dmpy)$_2$·(1)$_2$ (8): A solution of Zn(salphen) complex **1** (0.32 g, 0.530 mmol) in CH$_3$CN (30 mL) was combined with a solution of 2,6-pyridinedimethanol (43.6 mg, 0.313 mmol) in CH$_3$CN (10 mL). The mixture was heated to reflux for a short time (20 s) and then allowed to cool. The product crystallized upon standing, and two separate fractions were isolated. For both fractions (fraction 1: 53.6 mg; fraction 2: 42.6 mg) a mixture of the trinuclear assembly and demetalated **1** was evidenced by ^{1}H NMR spectroscopy. Recrystallization from cold hexane at –28 °C afforded analytically pure **8**. Total yield 96.2 mg (0.062 mmol, 40% based on **1**). The structure of the trinuclear assembly was further supported by X-ray diffraction. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.78 (s, 2 H, CH=N), 8.02 (d, ^4J = 2.5 Hz, 2 H, ArH), 7.84 (d, ^4J = 2.6 Hz, 2 H, ArH), 7.82 (d, ^4J = 2.4 Hz, 2 H, ArH), 7.72 (s, 2 H, CH=N), 6.98 (t, ^3J = 7.6 Hz, 2 H, ArH), 6.91 (d, ^4J = 2.5 Hz, 2 H, ArH), 6.77 (t, ^3J = 7.7 Hz, 2 H, Pyr-H), 6.67 (d, ^3J = 7.9 Hz, 2 H, ArH), 6.57 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.51 (d, ^3J = 7.8 Hz, 2 H, Pyr-H), 5.99 (t, ^3J = 7.4 Hz, 2 H, OH), 5.83 (d, ^3J = 7.6 Hz, 2 H, Pyr-H), 5.76 (d, ^3J = 7.6 Hz, 2 H, ArH), 5.67 (d, ^2J = 18.4 Hz, 2 H, CH_AH$_X$), 4.11 (d, ^2J = 18.4 Hz, 2 H, CH$_A$$H_X$), 4.04 (d, $^2J_{H,H}$ = 17.1, $^3J_{OH,H}$ = 6.8 Hz, 2 H, CH_BH$_Y$), 4.04 (d, $^2J_{H,H}$ = 17.1, $^3J_{OH,H}$ = 8.0 Hz, 2 H, CH$_B$$H_Y$), 2.08 [s, 18 H, C(CH$_3$)$_3$], 2.02 [s, 18 H, C(CH$_3$)$_3$], 1.70 [s, 18 H, C(CH$_3$)$_3$], 1.49 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 171.89, 171.28, 164.54, 164.28, 162.41, 157.22, 143.51, 143.07, 141.55, 141.50, 137.71, 136.02, 134.86, 129.90, 129.83, 128.68, 127.93, 125.90, 120.85, 119.74, 119.44, 117.60, 116.15, 116.11, 66.63, 62.19, 36.79, 36.40, 34.70, 34.48, 32.34, 32.15, 31.24, 30.93 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 806.3 [M – **1** – dmpy]$^+$ (calcd. 806.27), 602.4 [Zn complex **1**]$^+$ (calcd. 602.3). $C_{86}H_{108}N_6O_8Zn_3$ (1550.04): calcd. C 66.64, H 7.02, N 5.42; found C 66.90, H 7.11, N 5.45.

Trinuclear Assembly Zn(mmpy)$_2$·(1)$_2$ (9): This compound was prepared as described for assembly **8** by using **1** (0.43 g, 0.712 mmol) in CH$_3$CN (30 mL) and 2-(hydroxymethyl)-6-methylpyridine (58.8 mg, 0.477 mmol) in CH$_3$CN (10 mL). The product was isolated as a yellow to orange needle-shaped crystalline material (67.5 mg, 0.044 mmol, 19% based on mmpy). Subsequent crystallization fractions contained impure **9** with demetalated **1** being the only impurity. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.82 (s, 2 H, CH=N), 8.03 (d, ^4J = 2.6 Hz, 2 H, ArH), 7.84 (d, ^4J = 2.5 Hz, 2 H, ArH), 7.77 (s, 2 H, CH=N), 7.76 (d, ^4J not resolved, 2 H, ArH), 6.93 (t, ^3J = 7.2 Hz, 2 H, ArH), 6.88 (d, ^4J = 2.6 Hz, 2 H, ArH), 6.80 (t, ^3J = 7.7 Hz, 2 H, Pyr-H), 6.74 (d, ^3J = 7.7 Hz, 2 H, ArH), 6.57 (t, ^3J = 7.6 Hz, 2 H, ArH), 6.36 (d, ^3J = 8.0 Hz, 2 H, Pyr-H), 6.22 (d, ^3J = 7.4 Hz, 2 H, Pyr-H), 5.86 (d, ^3J = 7.5 Hz, 2 H, ArH), 5.53 (d, ^2J = 18.4 Hz, 2 H, CH_AH$_X$), 4.17 (d, ^2J = 18.4 Hz, 2 H, CH$_A$$H_X$), 2.17 [s, 18 H, C(CH$_3$)$_3$], 1.98 [s, 18 H, C(CH$_3$)$_3$], 1.73 [s, 18 H, C(CH$_3$)$_3$], 1.58 (s, 6 H, Pyr-CH$_3$), 1.53 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$): δ = 172.61, 172.50, 165.18, 162.21, 156.54, 143.48, 142.82, 141.10, 140.47, 139.22, 134.85, 133.91, 129.77, 129.70, 129.36, 129.31, 128.68, 127.53, 125.52, 122.00, 119.16, 118.95, 116.36, 114.64, 67.13, 36.85, 36.47, 34.75, 34.39, 32.38, 32.20, 30.95, 30.62, 22.66 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 790.3 [M – **1** – mmpy]$^+$ (calcd. 790.27), 602.4 [Zn complex **1**]$^+$ (calcd. 602.3). $C_{86}H_{108}N_6O_6Zn_3$ (1518.04): calcd. C 68.04, H 7.17, N 5.54; found C 67.55, H 7.10, N 5.43.

Trinuclear Assembly Zn(dmpy)$_2$·(2)$_2$ (10): This compound was prepared as described for assembly **8** by using **2** (422.5 mg, 0.859 mmol) in CH$_3$CN (25 mL) and 2,6-pyridinedimethanol (53.6 mg, 0.385 mmol) in CH$_3$CN (5 mL). The product was isolated as a yellow needle-shaped crystalline material (138.9 mg, 0.105 mmol, 54% based on dmpy). Subsequent crystallization fractions contained impure **10** with demetalated **2** being the only impurity. Crystals suitable for XRD were obtained by slow concentration of a C$_6$D$_6$ solution. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.52 (s, 2 H, CH=N), 7.80 (d, ^3J = 7.3, ^4J = 1.6 Hz, 2 H, ArH), 7.58 (d, ^3J = 7.3, ^4J = 1.6 Hz, 2 H, ArH), 7.56 (s, 2 H, CH=N), 7.47 (d, ^3J = 8.1 Hz, 2 H, ArH), 6.96 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.83–6.90 (m, 4 H, ArH and Pyr-H), 6.75–6.79 (m, 4 H, ArH), 6.72 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.60 (t, ^3J = 7.4 Hz, 2 H, ArH), 6.51 (d, ^3J = 7.8 Hz, 2 H, Pyr-H), 5.87 (d, ^3J = 7.6 Hz, 2 H, Pyr-H), 5.79 (d, ^3J = 7.8 Hz, 2 H, ArH), 5.63 (t, ^3J = 7.5 Hz, 2 H, OH), 5.54 (d, ^2J = 18.3 Hz, 2 H, CH_AH$_X$), 3.98 (d, ^2J = 18.2 Hz, 2 H, CH$_A$$H_X$), 3.87–3.98 (m, 4 H, Pyr-CH_2OH, overlapping signals), 2.02 [s, 18 H, C(CH$_3$)$_3$], 1.91 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$/C$_2$D$_2$Cl$_4$ = 6:4): δ = 173.30, 172.93, 164.86, 164.26, 163.48, 162.07, 157.04, 143.53, 143.46, 141.04, 140.81, 137.84, 134.87, 134.39, 131.87, 131.57, 128.68, 127.86, 126.15, 121.45, 120.82, 119.88, 117.91, 116.25, 116.03, 114.46, 113.47, 66.34, 62.19, 36.37, 36.01, 30.98, 30.67 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 982.5 [(**2**)$_2$]$^+$ (calcd. 982.32), 694.3 [M – **2** – dmpy]$^+$ (calcd. 694.14), 490.3 [Zn complex **2**]$^+$ (calcd. 490.16), 475.4 [Zn complex **2** – CH$_3$]$^+$ (calcd. 475.14). $C_{70}H_{76}N_6O_8Zn_3$ (1325.62): calcd. C 63.42, H 5.78, N 6.34; found C 63.52, H 5.93, N 6.39.

Trinuclear Assembly Zn(mmpy)$_2$·(2)$_2$ (11): This compound was prepared as described for assembly **8** by using **2** (0.51 g, 1.04 mmol) in CH$_3$CN (30 mL) and 2-(hydroxymethyl)-6-methylpyridine (86.0 mg, 0.698 mmol) in CH$_3$CN (5 mL). The product was isolated as a yellow to orange crystalline material (273.5 mg, 0.211 mmol, 61% based on mmpy). Subsequent crystallization fractions contained impure **11** with demetalated **2** being the only impurity. ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 8.56 (s, 2 H, CH=N), 7.81 (d, ^3J = 7.2, ^4J = 1.4 Hz, 2 H, ArH), 7.67 (s, 2 H, CH=N), 7.55 (m, 4 H, ArH), 6.97 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.83–6.89 (m, 6 H, ArH), 6.78 (t, ^3J = 7.7 Hz, 2 H, Pyr-H), 6.69 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.57 (t, ^3J = 7.5 Hz, 2 H, ArH), 6.35 (d, ^3J = 7.9 Hz, 2 H, Pyr-H), 6.17 (d, ^3J = 7.4 Hz, 2 H, Pyr-H), 5.83 (d, ^3J = 7.7 Hz, 2 H, ArH),

5.48 (d, ^2J = 18.4 Hz, 2 H, CH_AH$_X$), 4.21 (d, ^2J = 18.4 Hz, 2 H, CH$_A$$H_X$), 2.12 [s, 18 H, C(CH$_3$)$_3$], 1.92 [s, 18 H, C(CH$_3$)$_3$], 1.55 (s, 6 H, Pyr-CH$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6/$C_2D_2Cl_4$ = 6:4): δ = 174.02, 173.88, 164.88, 162.38, 161.89, 156.55, 143.60, 143.25, 140.88, 140.03, 139.34, 134.99, 134.77, 131.56, 131.25, 128.69, 127.64, 125.88, 122.21, 120.46, 120.26, 118.92, 116.68, 114.45, 113.44, 112.75, 67.01, 64.19, 36.48, 36.13, 30.85, 30.45, 22.63 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 679.3 [M – **2** – mmpy + H]$^+$ (calcd. 679.15), 678.3 [M – **2** – mmpy]$^+$ (calcd. 678.15), 490.3 [Zn complex **2**]$^+$ (calcd. 490.16), 475.3 [Zn complex **2** – CH$_3$]$^+$ (calcd. 475.14). $C_{70}H_{76}N_6O_6Zn_3$ (1293.62): calcd. C 64.99, H 5.92, N 6.50; found C 65.55, H 6.20, N 6.54.

Trinuclear Assembly Zn(dmpy)$_2$·(3)$_2$ (12): This compound was prepared as described for assembly **8** by using **3** (0.23 g, 0.350 mmol) in CH$_3$CN (25 mL) and 2,6-pyridinedimethanol (30.9 mg, 0.222 mmol) in CH$_3$CN (5 mL). The product was isolated as yellow needles (73.7 mg, 0.0447 mmol, 40% based on dmpy). Subsequent crystallization fractions contained impure **12** with demetalated **3** being the only impurity. ^{1}H NMR (400 MHz, C_6D_6): δ = 9.05 (s, 2 H, CH=N), 8.19 (d, ^4J = 2.2 Hz, 2 H, ArH), 8.02 (d, ^4J = 2.2 Hz, 2 H, ArH), 8.00 (s, 2 H, CH=N), 7.85 (d, ^4J = 2.4 Hz, 2 H, ArH), 7.79 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.56 (t, ^3J = 7.4 Hz, 2 H, ArH), 7.43 (t, ^3J = 7.5 Hz, 2 H, ArH), 7.33 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.15 (s, 2 H, ArH), 7.00 (d, ^4J = 2.4 Hz, 2 H, ArH), 6.67 (t, ^3J = 7.7 Hz, 2 H, Pyr-H), 6.21 (s, 2 H, ArH), 6.04 (t, ^3J = 7.3 Hz, 2 H, OH), 5.86 (d, ^3J = 7.8 Hz, 2 H, Pyr-H), 5.71 (d, ^3J = 7.5 Hz, 2 H, Pyr-H), 5.44 (d, ^2J = 18.3 Hz, 2 H, CH_AH$_X$), 4.09 (dd, $^2J_{H,H}$ = 17.0, $^3J_{OH,H}$ = 6.9 Hz, 2 H, CH_BH$_Y$), 4.09 (dd, $^2J_{H,H}$ = 16.1, $^3J_{OH,H}$ = 7.7 Hz, 2 H, CH$_B$$H_Y$), 3.77 (d, ^2J = 18.1 Hz, 2 H, CH$_A$$H_X$), 1.94 [s, 36 H, 2× C(CH$_3$)$_3$], 1.77 [s, 18 H, C(CH$_3$)$_3$], 1.48 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 171.89, 171.78, 165.39, 163.89, 163.44, 156.89, 143.70, 143.20, 141.71, 140.80, 137.72, 136.20, 134.85, 133.52, 132.30, 130.73, 130.61, 130.32, 130.05, 128.73, 127.32, 126.07, 125.84, 121.02, 119.90, 119.09, 117.63, 113.32, 113.04, 66.40, 61.80, 36.82, 36.33, 34.83, 34.50, 32.52, 32.09, 31.27, 30.63 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 856.4 [M – **3** – dmpy]$^+$ (calcd. 856.28), 652.4 [Zn complex **3**]$^+$ (calcd. 652.30), 637.5 [Zn complex **3** – CH$_3$]$^+$ (calcd. 637.28). $C_{94}H_{112}N_6O_8Zn_3$·1.5CH$_3$CN (1711.74): calcd. C 68.06, H 6.86, N 6.15; found C 67.67, H 6.79, N 5.88.

Trinuclear Assembly Zn(mmpy)$_2$·(3)$_2$ (13): This compound was prepared as described for assembly **8** by using **3** (0.35 g, 0.535 mmol) in CH$_3$CN (25 mL) and 2-(hydroxymethyl)-6-methylpyridine (44.3 mg, 0.360 mmol) in CH$_3$CN (5 mL). The product was isolated as an orange crystalline solid (154.3 mg, 0.0954 mmol, 53% based on mmpy). Subsequent crystallization fractions contained impure **13** with demetalated **3** being the only impurity. ^{1}H NMR (400 MHz, C_6D_6): δ = 9.14 (s, 2 H, CH=N), 8.20 (d, ^4J = 2.4 Hz, 2 H, ArH), 8.07 (d, ^4J = 2.3 Hz, 2 H, ArH), 8.05 (s, 2 H, CH=N), 7.78 (d, ^4J = 2.5 Hz, 2 H, ArH), 7.71 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.56 (t, ^3J = 7.3 Hz, 2 H, ArH), 7.42 (t, ^3J = 7.2 Hz, 2 H, ArH), 7.00 (d, ^4J = 2.5 Hz, 2 H, ArH), 6.68 (d, ^3J = 7.7 Hz, 2 H, Pyr-H), 6.32 (s, 2 H, ArH), 6.10 (d, ^3J = 7.4 Hz, 2 H, Pyr-H), 5.83 (d, ^3J = 8.0 Hz, 2 H, Pyr-H), 5.34 (d, ^2J = 18.4 Hz, 2 H, CH_AH$_X$), 3.74 (d, ^2J = 18.4 Hz, 2 H, CH$_A$$H_X$), 2.04 [s, 18 H, C(CH$_3$)$_3$], 1.92 [s, 18 H, C(CH$_3$)$_3$], 1.78 [s, 18 H, C(CH$_3$)$_3$], 1.69 (s, 6 H, Pyr-CH$_3$), 1.52 [s, 18 H, C(CH$_3$)$_3$] ppm; one signal (d, 2 H) overlaps with the solvent residual peak. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 173.07, 172.48, 164.60, 163.82, 162.99, 156.39, 143.87, 142.83, 140.96, 140.25, 139.21, 134.84, 134.22, 133.00, 132.09, 130.67, 130.48, 130.11, 129.85, 129.57, 128.69, 127.07, 126.05, 125.89, 122.13, 119.64, 119.35, 118.55, 113.32, 111.84, 66.95, 36.90, 36.37, 34.89, 34.43, 32.54, 32.14, 30.62, 22.62 ppm; two *t*Bu signals overlapping, i.e. C(*C*H$_3$)$_3$ resonances. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 840.4 [M – **3** – mmpy]$^+$ (calcd. 840.30), 652.4 [Zn complex **3**]$^+$ (calcd. 652.30), 637.5 [Zn complex **3** – CH$_3$]$^+$ (calcd. 637.28). $C_{94}H_{112}N_6O_6Zn_3$·CH$_3$CN (1659.21): calcd. C 69.49, H 6.99, N 5.91; found C 69.61, H 7.22, N 5.90.

Trinuclear Assembly Zn(dmpy)$_2$·(7)$_2$ (14): This compound was prepared as described for assembly **8** by using **7** (163.9 mg, 0.299 mmol) in CH$_3$CN (5 mL) and 2,6-pyridinedimethanol (28.4 mg, 0.204 mmol) in CH$_3$CN (5 mL). The product was isolated as a yellow crystalline solid (74.9 mg, 0.0521 mmol, 52% based on **7**). The ^{1}H and ^{13}C{^{1}H } NMR recorded for **7** in [D$_6$]benzene indicated the presence of two isomeric trinuclear assemblies. X-ray analysis of crystalline **7** showed only one of the possible isomers. Please note that the ^{1}H NMR spectrum for **14** is extremely difficult to interpret, and therefore the entire spectrum is given in the Supporting Information. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ = 173.47, 173.06, 173.02, 171.89, 171.25, 171.20, 164.47, 164.39, 164.25, 164.15, 163.72, 163.52, 162.41, 162.22, 162.12, 157.21, 157.14, 157.07, 143.74, 143.62, 143.51, 143.45, 143.30, 142.98, 142.93, 141.56, 141.36, 141.20, 141.13, 140.92, 137.87, 137.84, 136.03, 135.92, 135.03, 134.85, 134.71, 134.51, 131.88, 131.81, 131.61, 131.57, 129.99, 129.92, 129.81, 129.79, 128.68, 127.72, 126.23, 126.17, 125.93, 121.74, 121.65, 120.97, 120.74, 120.67, 119.86, 119.54, 119.40, 117.89, 117.83, 117.76, 116.37, 116.14, 116.05, 114.53, 114.42, 113.62, 113.43, 66.56, 66.48, 62.13, 36.76, 36.46, 36.38, 36.07, 34.66, 34.44, 32.28, 32.10, 31.23, 31.03, 30.85, 30.80 ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 1095 [(**7**)$_2$ + H]$^+$ (calcd. 1095.2), 760 [M – **7** – dmpy – CH$_3$ + Na]$^+$ (calcd. 760.2), 752 [M – **7** – dmpy]$^+$ (calcd. 752.2), 546 [Zn complex **7**]$^+$ (calcd. 546.2), 531 [Zn complex **7** – CH$_3$]$^+$ (calcd. 531.2). $C_{78}H_{92}N_6O_6Zn_3$ (1437.83): calcd. C 65.16, H 6.45, N 5.84; found C 65.32, H 6.56, N 5.82.

Mononuclear 1:1 Assembly 1·2-(Hydroxymethyl)pyridine (15): A mixture of complex **1** (0.38 g, 0.629 mmol) and 2-(hydroxymethyl)-pyridine (494.6 mg, 4.53 mmol) in CH$_3$CN (5 mL) was heated to reflux and then allowed to cool to ambient temperature. Orange, needle-shaped crystals deposited, which were isolated by filtration and dried. Yield 268.8 mg (0.377 mmol, 60% based on **1**). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.03 (s, 2 H, CH=N), 8.49 (d, ^4J = 4.7 Hz, 1 H, Pyr-H), 7.86 (t, ^3J =, ^4J = Hz, 1 H, Pyr-H), 7.81–7.84 (m, 2 H, ArH), 7.60 (d, ^3J = 7.9 Hz, 1 H, Pyr-H), 7.47 (d, ^4J = 2.7 Hz, 2 H, ArH), 7.32–7.34 (m, 2 H, ArH), 7.26–7.29 (m for ArH resolved, ^4J = 2.6 Hz, 3 H, overlapping ArH + Pyr-H), 4.65 (s, 2 H, Pyr-CH$_2$), 4.56 (br. s, 1 H, OH), 1.52 [s, 18 H, C(CH$_3$)$_3$], 1.35 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]acetone): δ = 171.88, 164.21, 149.60, 142.56, 141.29, 139.91, 130.44, 130.04, 128.86, 128.62, 128.38, 123.22, 122.00, 120.65, 119.50, 116.91, 64.19, 36.35, 34.52, 31.94, 30.44 ppm. ESI(+)-MS: *m*/*z* = 712.2 [M + H]$^+$ (calcd. 712.4), 625.2 (Zn complex **1** + Na)$^+$ (calcd. 625.3), 603.2 (Zn complex **1** + H)$^+$ (calcd. 603.3), 541.3 [**1**(H$_2$) + H]$^+$ (calcd. 541.4). $C_{42}H_{52}N_3O_3Zn$ (713.30): calcd. C 70.72, H 7.49, N 5.89; found C 70.81, H 7.55, N 5.86.

Mononuclear 1:1 Assembly 1·2-(2-Hydroxyethyl)pyridine (16): A mixture of complex **1** (0.37 g, 0.612 mmol) and 2-(2-hydroxyethyl)-pyridine (0.28 g, 2.27 mmol) in CH$_3$CN (5 mL) was heated to reflux and then allowed to cool to ambient temperature. Orange crystals deposited, which were isolated by filtration after 18 h and dried. Yield 207.9 mg (0.286 mmol, 47% based on **1**). ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 8.98 (s, 2 H, CH=N), 8.53 (d, ^3J = 4.6 Hz, 1 H, Pyr-H), 7.73–7.76 (m, 2 H, ArH), 7.61 (t, ^3J = 7.7, ^4J = 1.5 Hz, 1 H, Pyr-H), 7.56 (d, ^4J = 2.5 Hz, 2 H, ArH), 7.38 (d, *J* not resolved, 1 H, Pyr-H), 7.28–7.37 (m, 4 H, ArH), 7.07 (t, ^3J =

6.3 Hz, 1 H, ArH), 3.98 (br., 1 H, OH), 3.62 (t, ^3J = 5.4 Hz, 2 H, CH_2CH_2OH), 2.93 (t, ^3J = 6.1 Hz, 2 H, CH_2CH_2OH), 1.62 [s, 18 H, $C(CH_3)_3$], 1.40 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]acetone): δ = 171.98, 164.03, 161.21, 150.11, 142.54, 141.26, 138.64, 134.81, 130.34, 129.99, 128.86, 128.62, 128.38, 127.54, 125.73, 122.56, 119.41, 116.86, 62.08, 40.64, 36.36, 34.51, 31.94, 30.42 ppm. ESI(+)-MS: *m*/*z* = 726.3 $[M + H]^+$ (calcd. 726.4), 625.2 (Zn complex **1** + Na)$^+$ (calcd. 625.3), 603.2 (Zn complex **1** + H)$^+$ (calcd. 603.3), 541.3 [**1**(H$_2$) + H]$^+$ (calcd. 541.4). $C_{43}H_{55}N_3O_3Zn\cdot 1/2H_2O$ (736.34): calcd. C 70.14, H 7.67, N 5.71; found C 70.36, H 7.50, N 5.84.

Mixed Assembly 1·2-Bromo-6-methylpyridine/1·H$_2$O (17): A mixture of complex **1** (129.2 mg, 0.214 mmol) and 2-bromo-6-methylpyridine (377.7 mg, 2.01 mmol) in CH_3CN (5 mL) was heated to reflux and then allowed to cool to ambient temperature. Orange crystals deposited in due course, which were isolated by filtration after 18 h and dried. Yield 78.6 mg (0.109 mmol, 51% based on **1**). The compound cocrystallizes with the water-ligated system **1**·H$_2$O as a mixed dinuclear assembly. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.09 (s, 4 H, CH=N), 7.90–7.93 (m, 4 H, ArH), 7.74 (t, ^3J = 7.7 Hz, 1 H, pyridine-H$_{para}$), 7.55 (d, ^3J = 7.3 Hz, 1 H, pyridine-H$_{meta}$), 7.46 (d, *J* unresolved due to overlapping with other signal, 1 H, pyridine-H$_{meta}$), 7.45 (d, ^4J = 2.7 Hz, 4 H, ArH), 7.34–7.37 (m, 4 H, ArH), 7.25 (d, ^4J = 2.6 Hz, 4 H, ArH), 4.67 (d, ^3J = 5.8 Hz, 2 H, pyridine-CH_2), 4.59 (t, ^3J = 5.6 Hz, 1 H, CH_2OH), 1.55 [s, 36 H, $C(CH_3)_3$], 1.33 [s, 36 H, $C(CH_3)_3$] ppm. MALDI-TOF-MS (pyrene matrix): *m*/*z* = 710.4 [Zn complex **1**·Pyr – Br]$^+$ (calcd. 710.33), 602.3 (Zn complex **1**)$^+$ (calcd. 602.3), 587.4 [Zn complex **1** – CH_3]$^+$ (calcd. 587.3). $C_{78}H_{100}BrN_5O_6Zn_2\cdot CH_3CN$ (1455.43): calcd. C 66.02, H 7.13, N 5.77; found C 66.12, H 6.90, N 5.59.

Mononuclear Complex 1·2-Ethylpyridine (18): A combination of Zn(salphen) complex **1** (155.7 mg, 0.258 mmol) and 2-ethylpyridine (288.4 mg, 2.69 mmol) was dissolved in hot CH_3CN (10 mL). The orange solution was allowed to cool upon which orange block-shaped crystals separated. Filtration and drying of the crystalline material afforded 139.2 mg of product (0.196 mmol, 76% based on **1**). These crystals were suitable for X-ray diffraction studies. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 9.04 (s, 2 H, CH=N), 8.52 (d, ^3J = 5.3, ^4J = 0.8 Hz, 1 H, pyrine-H$_{ortho}$), 7.83–7.87 (m, 2 H, ArH), 7.77 (d, ^3J = 7.7, ^4J = 1.8 Hz, 1 H, pyrine-H$_{para}$), 7.46 (d, ^4J = 2.7 Hz, 2 H, ArH), 7.32–7.36 (m, 2 H, ArH), 7.30 (d, ^3J = 7.9 Hz, 1 H, pyridine-H), 7.26 (d, ^4J = 2.7 Hz, 2 H, ArH), 7.21 (t, ^3J = 6.4, ^4J = 1.1 Hz, 1 H, pyridine-H$_{meta}$), 2.74 (q, ^3J = 7.6 Hz, 2 H, CH_2CH_3), 1.53 [s, 18 H, $C(CH_3)_3$], 1.33 [s, 18 H, $C(CH_3)_3$], 1.03 (t, ^3J = 7.6 Hz, 3 H, CH_2CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]-acetone): δ = 173.60, 164.83, 164.13, 150.09, 143.10, 141.30, 139.78, 135.36, 131.68, 127.95, 124.28, 122.62, 120.67, 117.09, 113.57, 36.08, 30.69, 30.24, 14.65 ppm; some signals overlapping with residual solvent peaks. $C_{43}H_{55}N_3O_2Zn$ (711.33): calcd. C 72.61, H 7.79, N 5.91; found C 72.78, H 8.07, N 5.88.

Supporting Information (see footnote on the first page of this article): Copies of relevant NMR/MS spectra and additional crystallographic comments.

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93879 reflections unique R_{int} = 0.0484, GOF = 1.173, R_1 = 0.0630 and wR_2 = 0.1421 [$I > 2\sigma(I)$], min/max residual density = –1.986/1.966 e/Å^3. For **10**: $C_{82}H_{88}N_6O_8Zn_3$, M_r = 1481.69, monoclinic, $P2_1/n$, a = 20.0086(18), b = 17.028(2), c = 22.617(2) Å, β = 109.01°, V = 7285.2(14) Å^3, Z = 4, ρ = 1.351 mg/m^3, μ = 1.041 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 3104, crystal size 0.10 × 0.20 × 0.30 mm, θ(min) = 2.7°, θ(max) = 37.2°, 49944 reflections collected, 28313 reflections unique, GOF = 1.039, R_1 = 0.0680 and wR_2 = 0.1907 [$I > 2\sigma(I)$], min/max residual density = –1.433/2.093 e/Å^3. For **12**: $C_{96}H_{115}N_7O_8Zn_3$, M_r = 1691.13, triclinic, $P\bar{1}$, a = 15.3880(15), b = 16.7296(17), c = 18.4348(17) Å, α = 79.702(2), β = 88.982(5), γ = 68.221(7)°, V = 4329.9(7) Å^3, Z = 2, ρ = 1.297 mg/m^3, μ = 0.885 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1788, crystal size 0.02 × 0.05 × 0.20 mm, θ(min) = 2.51°, θ(max) = 31.2°, 47905 reflections collected, 28240 reflections unique, GOF = 0.912, R_1 = 0.0738 and wR_2 = 0.1776 [$I > 2\sigma(I)$], min/max residual density = –1.13/1.42 e/Å^3. For **14**: $C_{85.5}H_{103.25}N_{9.75}O_8Zn_3$, M_r = 1591.64, monoclinic, $C2/c$, a = 37.807(9) Å, b = 22.190(5) Å, c = 22.298(5) Å, β = 90.645(6)°, V = 18706(7) Å^3, Z = 8, ρ = 1.130 mg/m^3, μ = 0.816 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 6708, crystal size 0.30 × 0.10 × 0.03 mm, θ(min) = 2.59°, θ(max)= 30.85°, 28190 reflections collected, 17816 reflections unique R_{int} = 0.0972, GOF = 1.022, R_1 = 0.0712 and wR_2 = 0.1995 [$I > 2\sigma(I)$], min/max residual density –0.778/1.209 e/Å^3.

[16] A symmetrical complex of type $Zn(dmpy)_2(sac)_2$ was previously reported. This structure has two saccharinate (sac) counter anions and comprises two neutral dmpy ligands; see: V. T. Yilmaz, S. Guney, O. Andac, W. T. A. Harrison, *J. Coord. Chem.* **2003**, *56*, 21–32.

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[18] a) A. L. Singer, D. A. Atwood, *Inorg. Chim. Acta* **1998**, *277*, 157–162; b) A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2006**, *359*, 1807–1814; c) C. T. L. Ma, M. J. MacLachlan, *Angew. Chem. Int. Ed.* **2005**, *44*, 4178–4182.

[19] In earlier studies we have shown that upon coordination of pyridine donors to Zn(salphen) complexes the *ortho*-hydrogen atoms of the donor ligand undergo a diagnostic upfield shift; see for instance: E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 4256–4263. See also ref.[6b]

[20] Selected crystallographic data. For **15**: $C_{42}H_{53}N_3O_3Zn$, M_r = 713.24, monoclinic, $P2_1/c$, a = 14.4436(5), b = 10.4169(4), c = 25.7291(9) Å, β = 95.2300(10)°, V = 3855.0(2) Å^3, Z = 4, ρ = 1.229 mg/m^3, μ = 0.678 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1520, crystal size 0.60 × 0.40 × 0.30 mm, θ(min) = 3.18°, θ(max) = 39.7°, 20166 reflections collected, 16412 reflections unique (R_{int} = 0.0221), GOF = 1.034, R_1 = 0.0349 and wR_2 = 0.0956 [$I > 2\sigma(I)$], min/max residual density = –0.559/0.705 e/Å^3. For **16**: $C_{43}H_{55}N_3O_3Zn$, M_r = 727.27, monoclinic, $P2_1/c$, a = 12.9851(3), b = 25.1354(6), c = 11.9412(4) Å, β = 90.2910(10)°, V = 3897.39(18) Å^3, Z = 4, ρ = 1.239 mg/m^3, μ = 0.672 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1552, crystal size 0.40 × 0.30 × 0.10 mm, θ(min) = 2.82°, θ(max) = 38.20°, 75454 reflections collected, 21303 reflections unique (R_{int} = 0.0412), GOF = 1.036, R_1 = 0.0404 and wR_2 = 0.0996 [$I > 2\sigma(I)$], min/max residual density = –0.597/0.775 e/Å^3. For **17**: $C_{80}H_{102}BrN_6O_6Zn_2$, M_r = 1454.33, monoclinic, $P2_1/c$, a = 13.9816(5), b = 19.7417(9), c = 27.9420(11) Å, β = 102.513(2)°, V = 7529.4(5) Å^3, Z = 4, ρ = 1.283 mg/m^3, μ = 1.223 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 3068, crystal size 0.40 × 0.10 × 0.08 mm, θ(min) = 2.55°, θ(max) = 33.93°, 110509 reflections collected, 29388 reflections unique (R_{int} = 0.0572), GOF = 1.039, R_1 = 0.0577 and wR_2 = 0.1550 [$I > 2\sigma(I)$], min/max residual density = –2.112/1.687 e/Å^3. For **18**: $C_{43}H_{55}N_3O_2Zn$, M_r = 711.27, triclinic, $P\bar{1}$, a = 11.9979(10), b = 12.3620(9), c = 13.2589(8) Å, α = 87.308(3), β = 83.148(3), γ = 76.457(3)°, V = 1897.8(2) Å^3, Z = 2, ρ = 1.245 mg/m^3, μ = 0.686 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 760, crystal size 0.50 × 0.30 × 0.20 mm, θ(min) = 3.04°, θ(max) = 30.0°, 9773 reflections collected, 9013 reflections unique (R_{int} = 0.0201), GOF = 1.056, R_1 = 0.0298 and wR_2 = 0.0794 [$I > 2\sigma(I)$], min/max residual density = –0.271/0.444 e/Å^3.

[21] In the presence of bmpy (2-bromo-6-pyridinemethanol) complex **1** crystallizes from CH_3CN as a combination of **1**·H_2O and the O-ligated **1**·bmpy. We believe that this cocrystallization is caused by the hydrogen-bonding properties of the water ligand to adjacent Zn(salphen) complexes that consequently offers a better packing arrangement. For a related example, see ref.[11b]

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