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Isolation and Structural Characterization of a Binuclear Intermediate Species Pertinent to Transmetalation of Zn(salphen) Complexes and the Formation of Polynuclear Salen Structures

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Zinc(II) salphen complexes equipped with additional alkoxy donor groups at the 3-position of the salicylideneimine groups have been prepared to bind metal acetates in a second coordination sphere close to the central Zn(II) ion. The isolated binuclear monosalphen complexes have been studied in detail using NMR and MS techniques. Further synthesis has revealed that the formation of binuclear species from the parent salphen ligands is dependent on the nature of the bridging group between the two salicylideneimine groups and is prevented by replacement of one of the alkoxy substituents for a bulky *t*-Bu group. One of the binuclear Zn_2 complexes was crystallographically characterized and can be regarded as a structural model for the intermediate stage of the transmetalation of the central Zn(II) center within these dinuclear compounds by other metal acetate salts. Furthermore, the X-ray diffraction structure also relates well with some intermediate structural stages of the buildup of various polynuclear salen structures.

Introduction

Salen ligands and complexes play a profound role in homogeneous catalysis.[1] In the past decade, salen structures have, however, also emerged as highly useful components of various (supramolecular) materials,[2] among which are multimetallic systems for cooperative catalysis operations,[3] macrocyclic compounds,[4] and new templating systems.[5] For all of these materials, it is vital to understand and to exploit the reactivity and stability characteristics of the salen building blocks in order to fine-tune the material properties. Recently we have reported several studies devoted to the intriguing reactivity of the salphen [salphen = *N*,*N*′-phenylenebis(salicylideneimine)] family of Zn(II)-centered metallosalens.[6] The origin of this reactivity is found in the high Lewis acidity of the Zn(II) ion,[7] which allows strong binding of various N- and O-donor systems. On the other hand, the Zn(salphen) unit is kinetically labile, making it an excellent starting point for the introduction of various other metal ions by means of transmetalation (TM), as we have previously reported.[8]

The presence of supplementary hydroxyl and alkoxy substituents on the salen framework has been frequently used to assemble bimetallic monosalen complexes and catalysts.[9] We recognized the ability of such donor fragments to access bimetallic salphen complexes in order to be able to stabilize and analyze in detail the presumed binuclear intermediate

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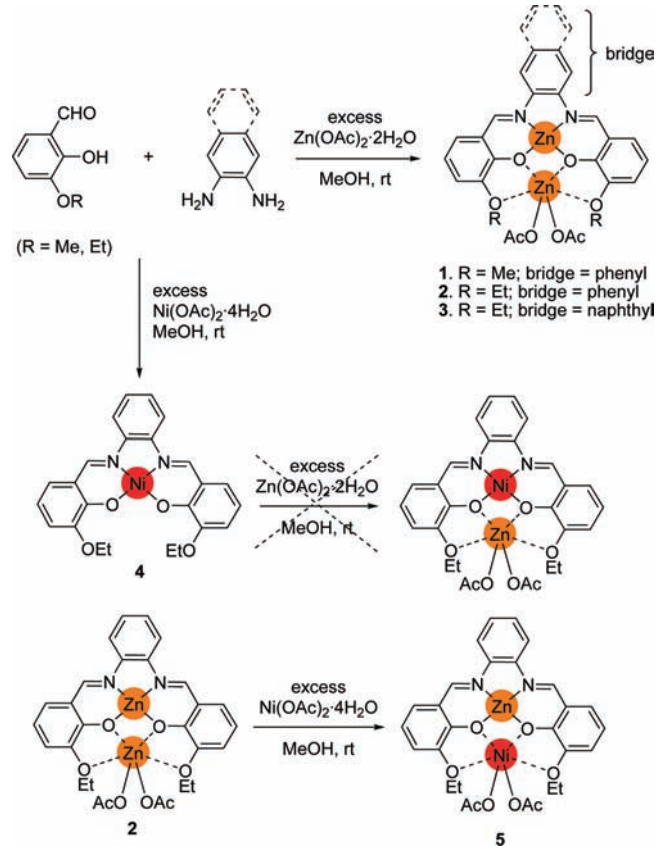
of our TM protocol.[8] Here, we report details about the synthesis and characterization of such binuclear complexes and their relation to the operative TM mechanism. Additionally, their resemblance with the key structural motifs found in the intermediates leading to polynuclear salen-based compounds is also discussed. Previously, MacLachlan and co-workers[10] reported on interesting bowl-shaped, macrocyclic heptanuclear Zn_7(trisalphen) cluster complexes, of which the central $[Zn_4O]^{6+}$ may be regarded as an attractive mimic for the active site of metalloenzymes such as phospholipase C that comprises a trinuclear zinc cluster.[11] The heptanuclear structures are built up from a central tri-Zn(salphen) unit. The hexa-hydroxy interior acts as a template for the creation of the $[Zn_4O]^{6+}$ cluster, and the cluster itself is held together via various OAc bridges between the different metal centers. Upon reaction with Co(II) acetate, a mixed metal assembly could be obtained in which the Zn ions within the central cluster were completely replaced by Co^{2+}. Another relevant example of a polynuclear salen structure in which an internal array of O atoms acts as a template for the formation of a trinuclear Zn_3 oxime-based system was provided by Nabeshima and co-workers.[12] Here, the authors suggested a cooperative mechanism for the formation of the trinuclear metallohost molecules. Two of the Zn(II) ions are inserted into the N_2O_2 salamo donor pockets, while a third Zn(II) ion is coordinated by two phenolic O atoms of the salen fragments and by two μ_2-acetato ligands that each bridge to one of the other Zn(II) centers, thereby completing their coordination sphere. The identification of the templating mechanism that leads to such polynuclear systems (cf. enzyme mimics) is thus intriguing, and suitable model systems could help to further understand the formation of such ensembles.

Results and Discussion

Homobimetallic complexes **1**−**3** (Scheme 1) were prepared in high isolated yields (76−98%) in a one-pot multistep synthesis using the appropriate diamine precursor, 3-RO-salicylaldehyde (R = Me, Et) and 2 equiv of $Zn(OAc)_2 \cdot 2H_2O$ (or excess) in MeOH. Compounds **1**−**3** proved to be sparingly soluble in many organic solvents except for DMSO and pyridine. NMR analysis was therefore performed in d_6-DMSO, and for all complexes, typical patterns were observed that can be associated with the formation of a Zn(II)-centered salphen complex (see the Supporting Information). Furthermore, the binuclear nature of **1**−**3** was supported by the presence of a singlet peak [integral ratio of $CH_3^{OEt}/CH_3^{OAc} = 1$] around 1.8 ppm that was ascribed to the OAc ligands of a $Zn(OAc)_2$ unit.[13] Convincing evidence for the formation of di-Zn(II) complexes was provided by MALDI-TOF mass spectrometry (see the Supporting Information). For instance, for **3**, a high-intensity peak was noted at $m/z = 641.0$, which corroborates with the fragment ion $[M - OAc]^+$. Other isotope clusters of low intensity were also found that are a result of the loss of the $Zn(OAc)_2$ fragment and dimerization of the mononuclear complex. Similar mass spectrometric results were obtained for complexes **1**−**2**.

Scheme 1. Synthesis of the Binuclear Salphen Complexes **1**−**3**, Ni Complex **4**, and Heterobimetallic Complex **5**



Fortunately, crystals of **2** suitable for X-ray diffraction could be obtained by dissolving the complex in hot MeOH and slowly cooling the obtained solution. The molecular structure for **2** is presented in Figure 1, a selection of bond distances/angles and crystallographic data can be found in Tables 1 and 2. The structure comprises a remarkable nonsymmetrical, bis-Zn-monosalphen complex in which the central metal center Zn(1) is in an approximate square-pyramidal geometry comprising a tetradentate N_2O_2 ligation

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(13) A similar NMR shift is noted for the OAc groups of non-complexed $Zn(OAc)_2 \cdot 2H_2O$ in the same solvent. This implies that DMSO is able to break up the binuclear complex, and observation of the non-assembled individual components is thus evident.

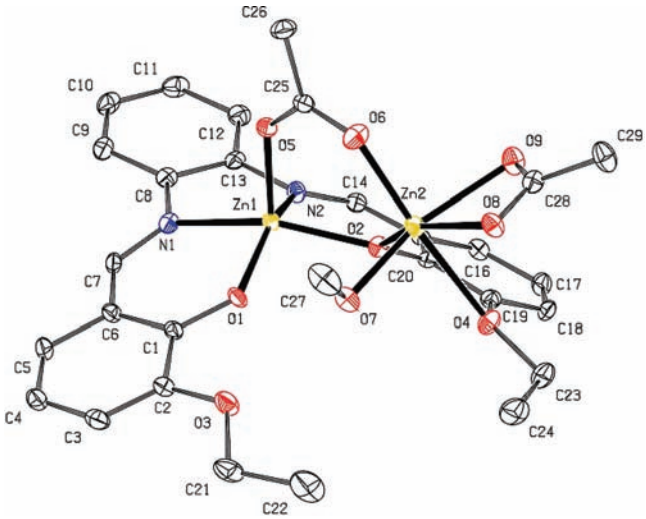


Figure 1. X-ray molecular structure determined for bimetallic complex **2**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Compounds **2** and **4** with esd's in Parentheses

2		**4**	
	Distances		
Zn(1)−O(1)	1.9890(17)	Ni(1)−O(1)	1.8485(6)
Zn(1)−O(2)	2.0263(18)	Ni(1)−O(2)	1.8439(6)
Zn(1)−O(5)	1.985(2)	Ni(1)−N(1)	1.8562(7)
Zn(1)−N(1)	2.077(2)	Ni(1)−N(2)	1.8569(6)
Zn(1)−N(2)	2.074(2)		
Zn(2)−O(2)	1.9903(19)		
Zn(2)−O(4)	2.475(2)		
Zn(2)−O(6)	2.010(2)		
Zn(2)−O(7)	2.0496(18)		
Zn(2)−O(8)	2.0723(18)		
Zn(2)−O(9)	2.1867(19)		
	Angles		
O(1)−Zn(1)−O(2)	93.65(7)	O(2)−Ni(1)−O(1)	83.43(3)
O(1)−Zn(1)−O(5)	105.35(9)	O(2)−Ni(1)−N(1)	178.64(3)
O(1)−Zn(1)−N(1)	89.32(8)	O(1)−Ni(1)−N(1)	95.31(3)
N(1)−Zn(1)−N(2)	78.40(8)	O(2)−Ni(1)−N(2)	95.34(3)
O(1)−Zn(1)−N(2)	148.64(9)	O(1)−Ni(1)−N(2)	178.70(3)
O(4)−Zn(2)−O(6)	166.29(7)	N(1)−Ni(1)−N(2)	85.92(3)
O(2)−Zn(2)−O(8)	154.32(9)		
O(7)−Zn(2)−O(9)	156.74(7)		

of the salphen ligand and one O atom of a bridging OAc. The other metal center, Zn(2), is positioned within the "second" coordination sphere of the salphen ligand via the O atoms of one of the OEt groups and one O donor of the N_2O_2 set. The rather distorted octahedral surrounding of Zn2 is completed by one bidentate OAc ligand, one bridging OAc, and one molecule of the crystallization solvent (MeOH). The Zn−O distance Zn(2)−O(4) is 2.475(2) Å and is considerably longer than the other Zn−O bond lengths. The bridging acetate ligand allows axial coordination of Lewis-acidic Zn(1) by O(5). As a consequence, the second Zn center (Zn(2)) becomes less symmetrically positioned; that is, it is pointing further away from O(4) within the distorted octahedral geometry and results in a significantly larger Zn−O bond length as compared to the other Zn−O distances involving Zn(2).

The structure of **2** (Figure 1) resembles (in part) the key structural unit found in the polysalen compounds reported by MacLachlan and co-workers[10] and Nabeshima and co-workers (see Figure 3).[12] In both examples, the formation of polynuclear Zn(II) complexes is mediated by the internal set of O-donor atoms of the salen ligand. Furthermore, the Zn center in both tetranuclear compound [Zn_4] and trinuclear [Zn_3] are held further in place by two bridging acetate ligands using the adjacent Lewis-acidic Zn(II) ions as anchoring points.

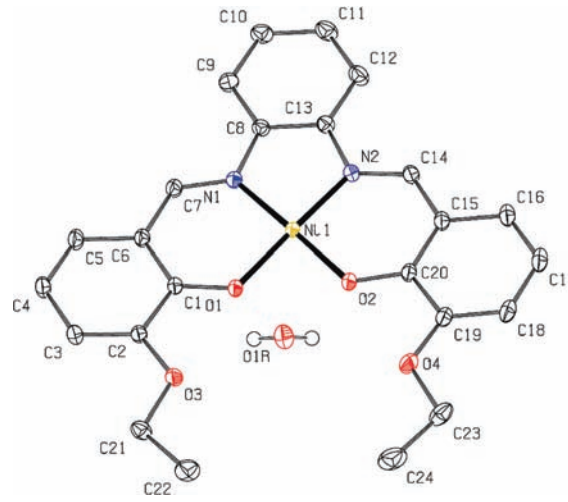


Figure 2. X-ray molecular structure determined for Ni(II) complex **4**. Hydrogen atoms are omitted for clarity except for the bonded water molecule.

The Lewis-acidic nature specifically found for the Zn(II) complexes of the present studies was supported by several additional experiments and analyses. First of all, under similar reaction conditions as reported for **1**−**3** (an excess of $Ni(OAc)_2 \cdot 4H_2O$ reagent), only the mono-Ni(II)salphen complex **4** (Scheme 1) was produced in high yield (84%). The X-ray molecular structure of **4** (Figure 2 and Tables 1 and 2) shows the expected square-planar arrangement of the salphen ligand around the Ni(II) center with a H_2O molecule trapped via H-bonding within the O_4 cavity. Treatment of **4** with 1 equiv of $Zn(OAc)_2 \cdot 2H_2O$ (or excess) in a mixture of $CHCl_3$/MeOH yielded unreacted **4** (Scheme 1). However, when binuclear complex **2** was treated with a slight excess of $Ni(OAc)_2 \cdot 4H_2O$ in THF at room temperature, formation of a new orange complex was observed.[14] Since both **2** (bright yellow) and **4** (deep red) have distinct and typical colors, the isolation of structure **5** (Scheme 1) was envisaged in which the $Ni(OAc)_2$ fragment is coordinated in a similar fashion as for the $Zn(OAc)_2$ fragment within bis-Zn(II) complexes **1**−**3**. When isolated **5** was subjected to NMR analysis, the color of the obtained solution immediately turned deep red, which is a strong indication for the (irreversible) formation of the Ni(II) complex **4**. Indeed, for several deuterated solvent systems (d_6-DMSO and d_5-pyridine) a fast transmetalation was confirmed, and no signals corresponding to **2** could be detected. In addition, the concomitant formation of 1 equiv (by signal integration) of $Zn(OAc)_2$ was evidenced by the presence of a sharp singlet resonance at 1.8 ppm in the ^{1}H NMR spectrum. Further proof for the presence of a mixed Zn−Ni salphen complex prior to transmetalation was offered by MALDI-TOF-MS, which

(14) Please note: heterogeneous reaction.

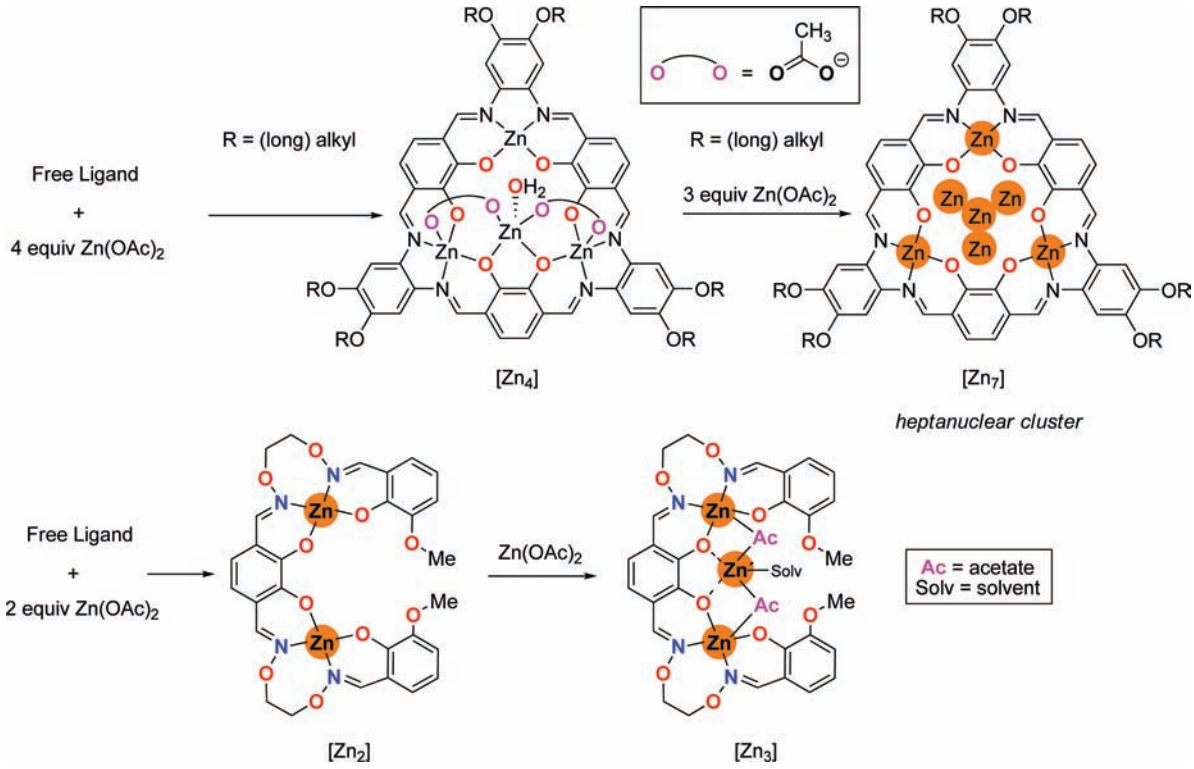


Figure 3. Schematic representation of the polynuclear salen complex formation reported by MacLachlan (at the top, $[Zn_4]$ and $[Zn_7]$) and Nabeshima (below, $[Zn_2]$ and $[Zn_3]$). Note the importance of both the array of internal O-donor atoms and the (bridging) acetate ligands.

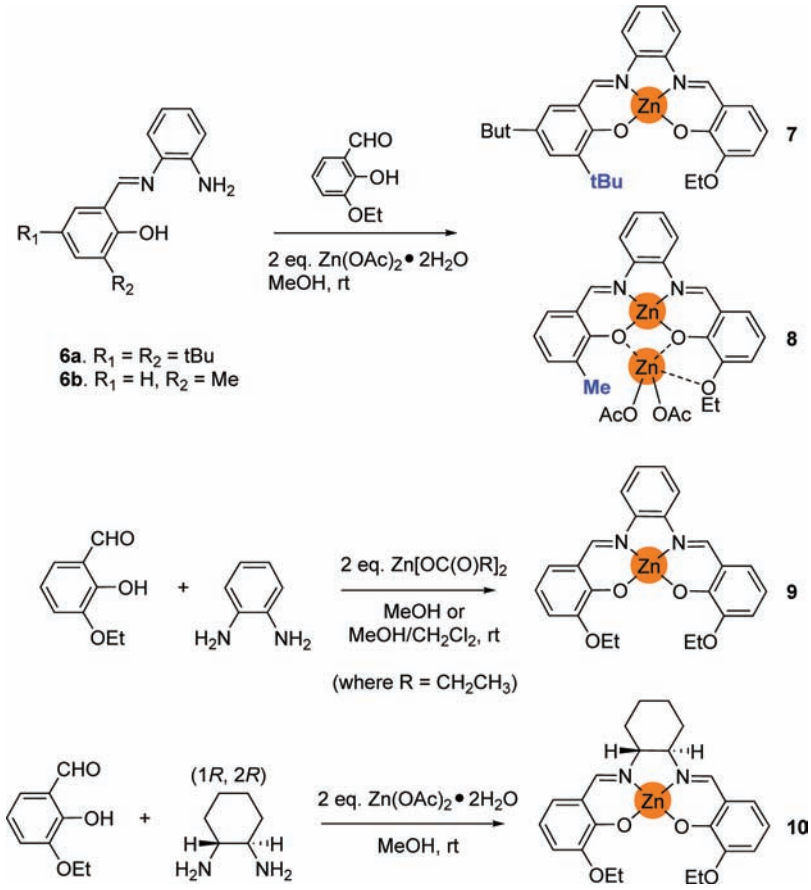
Table 2. Crystallographic Data and Structure Refinement for Complexes **2** and **4**

	complex **2**	complex **4**
empirical formula	$C_{29}H_{31}N_2O_9Zn_2$	$C_{26}H_{26}Cl_6N_2O_5Ni$
fw	682.30	717.90
temperature, K	100(2)	100(2)
wavelength, Å	0.71073	0.71073
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
unit cell dimensions (Å/deg)	$a = 7.7191(5)$, $\alpha = 87.326(3)$	$a = 9.2322(2)$, $\alpha = 90.7480(10)$
	$b = 13.3739(7)$, $\beta = 77.487(4)$	$b = 11.6101(3)$, $\beta = 95.5330(10)$
	$c = 14.4779(8)$, $\gamma = 78.697(3)$	$c = 14.4864(4)$, $\gamma = 107.2580(10)$
volume, Å^3	1430.80(14)	1474.52(6)
Z	2	2
density (calculated), Mg/m^3	1.584	1.617
abs coeff, mm^{-1}	1.734 mm^{-1}	1.242 mm^{-1}
$F(000)$	702	732
cryst size, mm^3	0.10 × 0.05 × 0.02	0.40 × 0.20 × 0.15
θ range for data collection, deg	2.88−31.14	2.83−39.29°
index ranges	$-11 \le h \le 9$, $-19 \le k \le 18$, $-20 \le l \le 20$	$-16 \le h \le 16$, $-20 \le k \le 18$, $-25 \le l \le 25$
refln collected/independent	22034, 8603 [R(int) = 0.0841]	36349, 15411 [R(int) = 0.0165]
completeness to θ max	92.9%	88.2%
abs correction	none	SADABS (Bruker-Nonius)
max. and min. transmission	0.9661, 0.8457	0.8356, 0.6365
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	8603/0/384	15411/0/371
goodness-of-fit on F^2	1.006	1.046
final R indices [$I > 2(I)$]	R1 = 0.0534, wR2 = 0.1133	R1 = 0.0306, wR2 = 0.0828
R indices (all data)	R1 = 0.0883, wR2 = 0.1283	R1 = 0.0347, wR2 = 0.0856
larg. diff. peak, hole, e Å^{-3}	0.860, −0.888	1.199, −1.235

showed a typical isotopic distribution at $m/z = 583.0$ corresponding to the fragment ion $[\mathbf{5} - OAc]^+$.[15]

Additional control compounds were then prepared (Scheme 2) to see whether the presence of both alkoxy groups is a prerequisite for binding of the $Zn(OAc)_2$ fragment. Monoimines **6a** and **6b** were prepared using a method developed by Atwood and co-workers.[16] The difference between these two monoimines is the bulkiness of the substitution at the 3-position of the salicylideneimine unit, which can have a large effect on the coordination ability of the Zn(salphen) complex to the $Zn(OAc)_2$ module. Complexes **7** and **8** were prepared in excellent isolated yields (86 and 87%, respectively) and their respective ^{1}H NMR spectra (recorded in d_6-DMSO) compared with those obtained for bimetallic species **1**−**3**. Remarkably, for **7**, no resonance was detected that could be assigned to an acetate fragment, and the other spectroscopic data clearly pointed at the formation of a *mono*-metallic species. Apparently, the bulky *t*-Bu group does not

Scheme 2. Synthesis of Zn(salphen) Complexes **7**−**10**



allow formation of the bimetallic compound. This was further confirmed by the isolation of **8**: here, the relatively small methyl group (Scheme 2) does not interfere with the formation and isolation of the bimetallic complex. The latter was completely characterized by a combination of analytical tools (see Experimental Section).

Two other complexes were also probed, namely, compounds **9** and **10** (Scheme 2). Interestingly, when the metalating reagent $Zn(OAc)_2$ was replaced for (excess) $Zn(propionate)_2$, selective isolation of mono-Zn(II) complex **9** (89%) was achieved. Although the X-ray molecular structure determined for **2** reveals ample room for the incorporation of a $Zn(propionate)_2$ module into the salphen structure, as observed for $Zn(OAc)_2$ (Figure 1), solubility features probably determine the course of the reaction.[17] Upon changing the bridging (rigid) phenyl unit for a more flexible cyclohexyl group (Scheme 2), again only mono-Zn(salen) **10** (69%) could be isolated. This result shows the importance of having a rigidified structure as a crucial prerequisite for bimetallic complex formation.

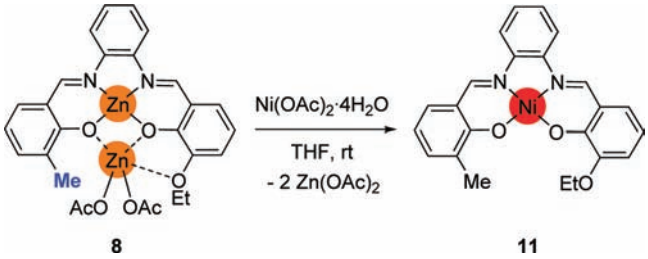
Bis-Zn(II) complex **2** contains two pending EtO groups that help to stabilize the bimetallic species. When treated with excess $Ni(OAc)_2 \cdot 4H_2O$, it is converted into the heterobimetallic Zn(II)−Ni(II) salphen complex **5**. The nonsymmetrical bis-Zn(II) complex **8** comprises only one of these stabilizing groups and therefore should be more prone to be directly converted into the transmetalation product, as opposed to **2**. Indeed, when **8** is treated under similar conditions (Scheme 3), a fast color change from yellow to deep red is observed, and complete dissolution of the initial solid material occurs, unlike observed for the conversion **2** → **5**. Analysis (NMR, MS) confirmed the exclusive formation of mono-Ni(II) complex **11** in high isolated yield (81%). The latter result demonstrates that complex **2** thus allows isolation of an intermediate stage of the transmetalation reaction.

(15) The location of this resonance corroborates well with the presence of $Zn(OAc)_2$. Note that (paramagnetic) $Ni(OAc)_2$ gives a broad signal around 2.8 ppm under these conditions. The Ni(II) species **4** is unable to bind $Zn(OAc)_2$ sufficiently strong, and consequently no heterobimetallic compound was isolated after the washing step with MeOH (see the Experimental Section). The latter observation plus the fact that **5** undergoes quantitative transmetalation upon dissolution to furnish **4** and 1 equiv of $Zn(OAc)_2$ is in line with the proposed formulation for **5** with a Ni/Zn stochiometry of 1:1. Furthermore, comparison of the solid-state IR spectra between bis-Zn(II)-(salphen) **2**, mono-Ni(II)salphen **4**, and complex **5** also revealed the formation of a unique complex (see Supporting Information). Isolated **5** was subjected to MALDI-TOF mass spectrometry: due to dissolution, some transmetalation could not be avoided, but nonetheless complex **5** was observed under the applied conditions. The mass spectrum also exhibited a peak at $m/z = 637.0$, which was ascribed to a bis-Ni(II) salphen complex and at 460.1 (attributed to Ni complex **4**). Finally, the elemental analysis carried out for **5** proved to be also in line with the proposed structure.

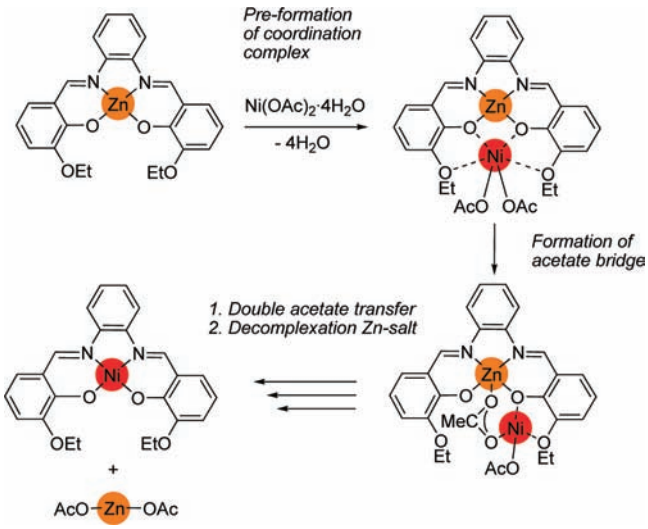
(16) Muñoz-Hernández, M.-A.; Keizer, T. S.; Parkin, S.; Patrick, B.; Atwood, D. A. *Organometallics* **2000**, *19*, 4416.

(17) Complex **9** is probably dimeric in nature because of the absence of sufficient steric bulk at the 3- positions of the salicylideneimine groups. See for instance:(a) Singer, A. L.; Atwood, D. A. *Inorg. Chim. Acta* **1998**, *277*, 157. Isolation of **9** should be interpretated as a (much) faster precipitation of dimer **9** versus the envisioned, bimetallic complex **9**·Zn(propionate)$_2$.

Scheme 3. Synthesis of Ni(salphen) **11** via Transmetalation of **8**



Scheme 4. Mechanistic Proposal for the Transmetalation of Zn(salphen) Complex **2** by $Ni(OAc)_2$



The combination of all of the spectroscopic/spectrometric and crystallographic results leads to the following mechanistic proposal (Scheme 4). First, an initial coordination complex is formed (cf., **5**), after which one of the OAc ligands of the $Ni(OAc)_2$ fragment bridges to the Lewis-acidic Zn(II) center (cf., X-ray structure of **2**). Then, double acetate transfer between the Ni and Zn center is anticipated. In the final stage, a $Zn(OAc)_2$ unit is expelled from the coordination sphere, and a mononuclear Ni(II)salphen complex is formed (cf., X-ray structure of **4** and NMR studies with complex **5**). This mechanism can also be projected onto the transmetalation of similar Zn(salphen) complexes using various other metal acetate salts.[8]

Conclusion

In summary, we here describe the isolation of bimetallic monosalphen structures that are relevant to both the transmetalation of Zn(salphen) complexes as well as the buildup of polynuclear compounds based on salen scaffolds.[9,10] The fundamental basis for the formation of bis-Zn−monosalphen complexes is the Lewis acidity of the central Zn ion. This allows the ligation of an axial ligand (i.e., OAc) and, therefore, isolation of bimetallic complexes **1**−**3**, **5**, and **8**. The in situ transmetalation of **2** affords mononuclear Ni(II) complex **4** (Scheme 3), which is coordinatively saturated and effectively will not provide stable binuclear species. Additional experiments have revealed that only one alkoxy group in the salphen structure is needed to provide bimetallic species. Furthermore, metalation of more flexible salen ligands incorporating, for instance, cyclohexyl bridges between the two salicylideneimine fragments provides only monometallic compounds, underlining the importance of rigidity for bimetallic complex formation. The rigidity of the salphen system leads to increased Lewis acidity behavior of the Zn(II) ion: the Zn center is forced into an unfavorable square-planar geometry, which increases its Lewis acidic behavior. This was previously supported by PM3 calculations that allowed access to the potential energy surface of Zn(salphen) derivatives and showed a localized positive charge on the Zn center. This Lewis acidity allows strong axial binding of axial ligands (cf., carboxylates and N-donor ligands).[7] These specific properties of the Zn(salphen) family of complexes help to further rationalize the formation and reactivity of heptanuclear Zn_7 cluster compounds based on a trisalphen macrocycle that was recently reported by MacLachlan et al.[10] The three central Zn ions template a stepwise construction of the central $[Zn_4O]^{6+}$ unit through a sequence of axial coordination/bridging of the OAc ligands and deprotonation of a single H_2O ligand. A similar reasoning may be applied for a trinuclear oxime-based salen structure reported by Nabeshima et al.[12] Our current focus is on the stepwise introduction of different metal ions in polysal(ph)en structures using our developed TM protocol to afford (catalytically active) heteromultimetallic complexes useful for multistep organic syntheses.

Experimental Section

General Comments. All starting materials were purchased from commercial sources and used without further purification. Compound **6a** was prepared using a previously reported method.[15] Elemental analyses were performed at the Unidad de Análisis Elemental of the University of Santiago de Compostela (Spain). All NMR measurements were carried out on a Bruker-400 MHz spectrometer at ambient temperature unless stated otherwise, and chemicals shifts are given in parts per million versus TMS. Mass spectrometric data were obtained from the Research Support unit of the ICIQ, and MALDI-TOF experiments were carried out with pyrene as a matrix. IR spectra (solid state) were recorded on a Bruker Tensor 27 apparatus.

Synthesis of [Zn(3-MeO-salphen)]·[Zn(OAc)$_2$] (1). To a solution of 1,2-diaminobenzene (253.9 mg, 2.34 mmol) and 3-methoxysalicylaldehyde (920.0 mg, 6.05 mmol) in MeOH (40 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (1.39 g, 6.33 mmol) in MeOH (20 mL). The initial orange solution turned immediately yellow, and a yellow solid started to precipitate rapidly. The product was collected by filtration after 6 h and dried to furnish 1.48 g of **1** (2.30 mmol, 98%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.01 (s, 2H, CH=N), 7.89−7.91 (m, 2H, ArH), 7.38−7.40 (m, 2H, ArH), 7.05 (d, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2H, ArH), 6.87 (d, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 2H, ArH), 6.47 (t, ^3J = 7.8 Hz, 2H, ArH), 3.77 (s, 6H, OMe), 1.81 (s, 6H, OAc). ^{13}C{^{1}H} NMR (100 MHz, 80/20 v/v d_5-pyridine/d_6-DMSO): δ 178.79, 165.32, 164.38, 153.93, 140.89, 128.70, 128.32, 120.07, 117.56, 115.16, 113.33, 56.19, 23.59. MS (MALDI-TOF, pyrene matrix): *m/z* 563.1 (M − OAc)$^+$, 903.1 (2 × [M − Zn(OAc)$_2$] + Na)$^+$, 1003.1 (2 × [M − Zn(OAc)$_2$] + Zn(OAc)]$^+$, 1085.1 (M + [M − Zn(OAc)$_2$] + Na]$^+$. Anal. calcd for $C_{26}H_{24}N_2O_8Zn_2 \cdot 2H_2O$: C, 47.36; H, 4.28; N, 4.25. Found: C, 47.38; H, 4.11; N, 4.20.

Synthesis of [Zn(3-EtO-salphen)]·[Zn(OAc)$_2$] (2). To a solution of 1,2-diaminobenzene (0.56 g, 5.18 mmol) and 3-ethoxysalicylaldehyde (2.23 g, 13.42 mmol) in MeOH (130 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (2.56 g, 11.66 mmol) in MeOH (20 mL). The initial orange solution turned immediately yellow, and a yellow solid started to precipitate rapidly. The product was collected

by filtration after 2 h and dried to furnish 3.48 g of **2** (4.83 mmol, 95%). Crystals suitable for X-ray analysis were obtained from hot MeOH. ^{1}H NMR (400 MHz, d_6-DMSO): δ = 9.01 (s, 2H, CH═N), 7.88−7.90 (m, 2H, ArH), 7.37−7.39 (m, 2H, ArH), 7.05 (d, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 2H, ArH), 6.87 (d, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, ArH), 6.42 (t, ^3J = 7.7 Hz, 2H, ArH), 4.05 (q, ^3J = 7.0 Hz, 4H, OCH_2CH$_3$), 1.81 (s, 6H, OAc), 1.37 (t, ^3J = 7.0 Hz, 6H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, 80/20 v/v d_5-pyridine/d_6-DMSO): δ 178.81, 165.83, 164.36, 153.05, 140.86, 129.19, 128.31, 120.43, 117.79, 117.55, 113.41, 65.07, 23.57, 15.93. MS (MALDI-TOF, pyrene matrix): *m/z* 466.2 [M − Zn(OAc)$_2$]$^+$, 489.2 [M − Zn(OAc)$_2$ + Na]$^+$, 505.1 [M − Zn(OAc)$_2$ + K]$^+$, 591.1 (M − OAc)$^+$, 857.0 (M + Zn(OAc)$_2$ + Na)$^+$, 1302.08 (2M)$^+$. Anal. calcd for $C_{28}H_{28}N_2O_8Zn_2\cdot1.5H_2O$: C, 49.57; H, 4.61; N, 4.13. Found: C, 49.92; H, 4.55; N, 4.10.

Synthesis of [Zn(3-EtO-salnaph)]·[Zn(OAc)$_2$] (3). To a solution of 2,3-diaminonaphthalene (38.3 mg, 0.242 mmol) and 3-ethoxy-salicylaldehyde (91.4 mg, 0.550 mmol) in MeOH (20 mL) was added a solution of Zn(OAc)$_2\cdot2H_2O$ (156.4 mg, 0.713 mmol) in MeOH (5 mL). The initial orange solution turned immediately yellow, and a yellow solid started to precipitate rapidly. The product was collected by filtration after 16 h and dried to furnish 132.7 mg of **3** (0.184 mmol, 76%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.16 (s, 2H, CH═N), 8.34 (s, 2H, ArH), 7.94−7.96 (m, 2H, ArH), 7.51−7.53 (m, 2H, ArH), 7.09 (d, ^3J = 8.1 Hz, ^4J = 1.4 Hz, 2H, ArH), 6.90 (d, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 2H, ArH), 6.45 (t, ^3J = 7.7 Hz, 2H, ArH), 4.07 (q, ^3J = 7.0 Hz, 4H, OCH_2CH$_3$), 1.85 (s, 6H, OAc), 1.38 (t, ^3J = 7.0 Hz, 6H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, 80/20 v/v d_5-pyridine/d_6-DMSO): δ 178.64, 166.18, 165.48, 152.99, 140.52, 133.34, 129.28, 128.85, 127.22, 120.61, 118.09, 115.03, 113.43, 65.04, 23.55, 15.99. MS (MALDI-TOF-MS, pyrene matrix): *m/z* 539.1 [M − Zn(OAc)$_2$ + Na]$^+$, 641.0 [M − OAc]$^+$, 823.0 [M + (Zn(OAc)$_2$ + Zn(OAc)]$^+$, 907.0 [M + 2 × Zn(OAc)$_2$ + Na]$^+$, 1009.2 [2 × M − EtH + H]$^+$, 1073.2 [2 × {M − Zn(OAc)$_2$} + K]$^+$. Anal. calcd for $C_{32}H_{30}N_2O_8Zn_2\cdot2.5H_2O$: C, 51.49; H, 4.73; N, 3.75. Found: C, 51.58; H, 4.56; N, 3.79.

Synthesis of [Ni(3-EtO-salphen)] (4). To a solution of 1,2-diaminobenzene (0.20 g, 1.85 mmol) and 3-ethoxy-salicylaldehyde (0.63 g, 3.79 mmol) in MeOH (30 mL) was added a solution of Ni(OAc)$_2\cdot4H_2O$ (0.99 g, 3.98 mmol) in MeOH (15 mL). The initial mixture was stirred for 16 h, and then the microcrystalline dark brown product was collected by filtration and dried. Yield: 716.6 mg (1.55 mmol, 84%). Crystals suitable for X-ray diffraction were obtained from $CHCl_3$. ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.88 (s, 2H, CH═N), 8.16−8.18 (m, 2H, ArH), 7.33−7.36 (m, 2H, ArH), 7.23 (d, ^3J = 8.2 Hz, ^4J = 1.4 Hz, 2H, ArH), 6.89 (d, ^3J = 7.5 Hz, ^4J = 1.4 Hz, 2H, ArH), 6.57 (t, ^3J = 7.8 Hz, 2H, ArH), 4.03 (q, ^3J = 6.9 Hz, 4H, OCH_2CH$_3$), 1.34 (t, ^3J = 7.0 Hz, 6H, OCH$_2$CH_3). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 2H, CH═N), 7.72−7.74 (m, 2H, ArH), 7.21−7.23 (m, 2H, ArH), 6.95 (d, ^3J = 8.1 Hz, 2H, ArH), 6.75 (d, ^3J = 6.8 Hz, 2H, ArH), 6.56 (t, ^3J = 7.8 Hz, 2H, ArH), 4.07 (q, ^3J = 6.9 Hz, 4H, OCH_2CH$_3$), 1.55 (t, ^3J = 6.9 Hz, 6H, OCH$_2$CH_3). The product is too insoluble for a ^{13}C{^{1}H} NMR analysis. MS (MALDI-TOF, pyrene matrix): *m/z* 483.0 [M + Na]$^+$, 943.1 (2 M + Na)$^+$. Anal. calcd for $C_{24}H_{22}N_2O_4Ni\cdot1/2H_2O$: C, 61.31; H, 4.93; N, 5.96. Found: C, 61.20; H, 4.82; N, 5.72.

Mixed Zn−Ni Complex (5). Complex **2** (98.1 mg, 0.143 mmol) was suspended in THF (10 mL), and then Ni(OAc)$_2\cdot4H_2O$ (47.7 mg, 0.192 mmol) was added. The initial yellowish suspension was stirred for 18 h, concentrated, and triturated with MeOH. The residue was dried to yield an orange to brown solid (53.8 mg, 0.0835 mmol, 55%). ^{1}H NMR analysis was performed in both d_6-DMSO and d_5-pyridine, affording exclusively (after dissolution) complex **4** (see its ^{1}H NMR data) and 1 equiv of Zn(OAc)$_2$ (δ 1.8). MALDI-TOF-MS (pyrene matrix): *m/z* 637.0 [M$^+$, bis-Ni(II) complex, calcd. 637.06], 583.0 [(M − OAc)$^+$, Zn/Ni complex, calcd. 583.04], 499.0 [(M + K)$^+$, mono-Ni complex, calcd. 499.06], 483.1 [(M + Na)$^+$, mono-Ni complex, calcd. 483.08], 460.1 [M$^+$, mono-Ni complex, calcd. 460.09]. IR (neat, cm^{-1}): 3035, 2970, 2931, 1738, 1633, 1612, 1585, 1555, 1500, 1459, 1394, 1378, 1323, 1294, 1254, 1211, 1179, 1120, 1097, 1026, 922, 778, 756, 733, 663. Anal. calcd for $C_{28}H_{28}N_2O_8NiZn\cdot1/2H_2O$: C, 51.45; H, 4.47; N, 4.29. Found: C, 51.33; H, 4.55; N, 4.28.

Synthesis of Monoimine (6b). A mixture of 3-methyl-salicylaldehyde (1.00 g, 7.34 mmol) and 1,2-diaminobenzene (0.91 g, 8.42 mmol) in MeOH (30 mL) was stirred for 3 h and then cooled to −25 °C, upon which the product crystallized. Filtration and drying afforded yellow/orange needles of **6b** (0.41 g, 25%). Subsequent fractions yielded mixtures of the mono- and bis-imine products. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.28 (s, 1H, OH), 8.64 (s, 1H, CH═N), 7.38 (d, ^3J = 7.6 Hz, 2H, ArH), 7.13 (t, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, ArH), 7.07 (d, ^3J = 8.2 Hz, ^4J = 1.5 Hz, 1H, ArH), 6.90 (t, ^3J = 7.5 Hz, 1H, ArH), 6.80−6.84 (m, 2H, ArH), 4.04 (s, 2H, NH_2), 2.35 (s, 3H, Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.36, 159.06, 140.84, 135.37, 134.12, 129.97, 128.05, 126.13, 118.84, 118.80, 118.39, 115.80, 15.52. MS (ESI): *m/z* 227.1 (M + H)$^+$. Anal. calcd for $C_{14}H_{14}N_2O\cdot1/5\ H_2O$: C, 73.15; H, 6.31; N, 12.19. Found: C, 73.31; H, 6.31; N, 12.24.

Synthesis of Nonsymmetrical [Zn(3-EtO-salphen)] (7). To a solution of 3-ethoxy-salicylaldehyde (0.15 g, 0.90 mmol) and the monoimine **6a** (0.23 g, 0.71 mmol) in MeOH (30 mL) was added a solution of Zn(OAc)$_2\cdot2H_2O$ (0.45 g, 2.05 mmol) in MeOH (10 mL). The initial orange-colored solution was stirred for 18 h and then filtered, and the residue was dried to furnish complex **7** as a yellow to orange solid (327.0 mg, 0.61 mmol, 86%). ^{1}H NMR (400 MHz, d_6-acetone/d_5-pyridine, 90:10 v/v): δ 9.05 (s, 1H, CH═N), 9.04 (s, 1H, CH═N), 7.74−7.84 (m, 2H, ArH), 7.51 (d, ^4J = 2.7 Hz, 1H, ArH), 7.31−7.36 (m, 2H, ArH), 7.28 (d, ^4J = 2.6 Hz, 1H, ArH), 7.14 (d, ^3J = 8.0 Hz, ^4J = 1.7 Hz, 1H, ArH), 7.00 (d, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 1H, ArH), 6.46 (t, ^3J = 7.7 Hz, 1H, ArH), 4.35 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 1.60 (s, 9H, C(CH$_3$)$_3$), 1.37 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3), 1.34 (s, 9H, C(CH$_3$)$_3$). ^{13}C{^{1}H} NMR (100 MHz, d_5-pyridine): δ 172.60, 172.30, 167.47, 164.47, 163.79, 153.36, 142.80, 141.48, 141.03, 135.18, 130.72, 130.50, 130.35, 128.20, 127.72, 122.56, 121.35, 119.76, 117.19, 113.38, 66.51, 36.69, 34.72, 32.31, 30.71, 16.58. MS (MALDI-TOF, pyrene matrix): *m/z* 534.3 (M)$^+$, 1070.4 (2M)$^+$. Anal. calcd for $C_{30}H_{34}N_2O_3Zn\cdot1/3MeOH$: C, 66.64; H, 6.51; N, 5.12. Found: C, 66.69; H, 6.74; N, 5.23.

Synthesis of Nonsymmetrical [Zn(3-EtO-salphen)]·[Zn(OAc)$_2$] (8). To a solution of monoimine **6b** (0.38 g, 1.68 mmol) and 3-ethoxy-salicylaldehyde (0.29 g, 1.75 mmol) in MeOH (40 mL) was added a solution of Zn(OAc)$_2\cdot2H_2O$ (0.88 g, 4.01 mmol) in MeOH (10 mL). A yellow solution was initially obtained, and after 10 min, a suspension was noted. The product was collected by filtration after 2 h and dried to yield **8** as a yellow solid (912.1 mg, 1.46 mmol, 87%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.99 (s, 1H, CH═N), 8.98 (s, 1H, CH═N), 7.87−7.89 (m, 2H, ArH), 7.36−7.39 (m, 2H, ArH), 7.28 (d, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 1H, ArH), 7.20 (d, ^3J = 6.8 Hz, 1H, ArH), 7.06 (d, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 1H, ArH), 6.88 (d, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 1H, ArH), 6.44 (t, ^3J = 7.4 Hz, 1H, ArH), 6.41 (t, ^3J = 7.7 Hz, 1H, ArH), 4.09 (q, ^3J = 7.0 Hz, 2H, OCH_2CH$_3$), 2.20 (s, 3H, Ar-CH$_3$), 1.81 (s, 6H, OAc), 1.37 (t, ^3J = 7.0 Hz, 3H, OCH$_2$CH_3). ^{13}C{^{1}H} NMR (100 MHz, d_5-pyridine): δ 179.20, 173.12, 166.70, 164.15, 164.07, 153.38, 141.09, 141.06, 135.63, 135.09, 132.51, 129.56, 128.16, 128.10,

120.85, 119.68, 119.43, 117.30, 117.27, 114.12, 113.41, 65.67, 23.57, 18.52, 16.06. MS (MALDI-TOF, pyrene matrix): *m*/*z* 459.1 $[M - Zn(OAc)_2 + Na]^+$, 899.0 $[2\ M - 2 \times Zn(OAc)_2 + Na]^+$. Anal. calcd for $C_{27}H_{26}N_2O_7Zn_2 \cdot 1.5H_2O$: C, 50.02; H, 4.51; N, 4.32. Found: C, 50.32; H, 4.36; N, 4.37.

Synthesis of [Zn(3-EtO-salphen)] (9). To a solution of 1,2-diaminobenzene (0.19 g, 1.76 mmol) and 3-ethoxy-salicylaldehyde (0.59 g, 3.55 mmol) in MeOH (80 mL) was added $Zn(propionate)_2$ (1.00 g, 4.73 mmol) dissolved in warm MeOH (50 mL). The initial reaction mixture was heated to reflux and then allowed to cool to ambient temperature. After 16 h, the obtained suspension was filtered and the residue dried to furnish a yellow to orange solid (732.5 mg, 1.57 mmol, 89%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 9.01 (s, 2H, CH═N), 7.88−7.90 (m, 2H, ArH), 7.37−7.39 (m, 2H, ArH), 7.05 (d, ^3J = 8.1 Hz, ^4J = 1.6 Hz, 2H, ArH), 6.87 (d, ^3J = 7.5 Hz, ^4J = 1.6 Hz, 2H, ArH), 6.42 (t, ^3J = 7.7 Hz, 2H, ArH), 4.05 (q, ^3J = 7.0 Hz, 4H, OCH_2CH_3), 1.37 (t, ^3J = 7.0 Hz, 6H, OCH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, d_5-pyridine): δ 166.55, 163.95, 153.42, 150.70, 140.98, 136.30, 129.17, 128.01, 124.28, 120.54, 118.68, 117.16, 113.35. MS (MALDI-TOF): *m*/*z* = 466.3 $(M)^+$. Anal. calcd for $C_{24}H_{22}N_2O_4Zn \cdot H_2O$: C, 59.33; H, 4.98; N, 5.77. Found: C, 59.06; H, 5.22; N, 5.77.

Synthesis of [Zn(3-EtO-salen)] (10). A homogeneous mixture of (1*R*,2*R*)-1,2-diaminocyclohexane (68.3 mg, 0.598 mmol), 3-ethoxy-salicylaldehyde (0.20 g, 1.20 mmol), $Zn(OAc)_2 \cdot 2H_2O$ (0.42 g, 1.91 mmol), and NEt_3 (5 mL) in MeOH (40 mL) was shortly heated to reflux. Then, the mixture was allowed to cool and was further stirred for 2 h at ambient temperature, after which the mixture was filtered and the solid residue dried to furnish **10** as a light yellow solid (195.6 mg, 0.413 mmol, 69%). ^{1}H NMR (400 MHz, $CDCl_3$ + 10% v/v d_5-pyridine): δ 8.28 (s, 2H, CH═N), 6.77−6.82 (m, 4H, ArH), 6.44 (t, ^3J = 7.7 Hz, 2H, ArH), 4.21 (m, 2H, −C*H*−N═C), 4.05−4.10 (m, 4H, OCH_2CH_3), 3.06 (br, 2H, cyclohexyl-H), 2.37 (br, 2H, cyclohexyl-H), 1.93 (br, 2H, cyclohexyl-H), 1.46 (t, ^3J = 6.7 Hz, 6H, OCH_2CH_3), 1.34 (br, 2H, cyclohexyl-H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$ + 10% v/v d_5-pyridine): δ 164.71, 151.89, 126.45, 118.21, 114.81, 111.41, 64.87, 63.89, 27.76, 23.93, 14.57. MS (MALDI-TOF): *m*/*z* 472.2 $(M)^+$, 495.2 $(M + Na)^+$, 947.3 $(2M + H)^+$, 971.3 $(2M + Na)^+$. Anal. calcd for $C_{24}H_{28}N_2O_4Zn \cdot 2H_2O$: C, 56.53; H, 6.33; N, 5.49. Found: C, 56.49; H, 6.02; N, 5.42.

Synthesis of Nonsymmetrical [Ni(3-EtO-salphen)] (11). To a suspension of complex **8** (147.1 mg, 0.224 mmol) in THF (15 mL) was added a suspension of $Ni(OAc)_2 \cdot 4H_2O$ (63.4 mg, 0.255 mmol) in THF (5 mL). Upon addition of the Ni reagent, the reaction mixture turned deep red over time (1−2 h), and complete dissolution was noted. After 3 h, the solution was concentrated and triturated with MeOH (25 mL) and filtered and the residue dried to give a brown solid. Yield: 77.9 mg (0.181 mmol, 81%). ^{1}H NMR (400 MHz, d_6-DMSO): δ 8.88 (s, 1H, CH═N), 8.87 (s, 1H, CH═N), 8.15−8.17 (m, 2H, ArH), 7.46 (d, ^3J = 7.4 Hz, ^4J = 1.3 Hz, 1H, ArH), 7.33−7.36 (m, 2H, ArH), 7.23−7.27 (m, 2H, ArH), 6.91 (d, ^3J = 7.4 Hz, ^4J = 1.6 Hz, 1H, ArH), 6.54−6.61 (m, 2H, ArH), 4.12 (q, ^3J = 7.0 Hz, 2H, OCH_2CH_3), 2.16 (s, 3H, Ar-CH_3), 1.30 (t, ^3J = 7.0 Hz, 3H, OCH_2CH_3). ^{13}C{^{1}H} NMR (100 MHz, d_6-DMSO/d_6-benzene 90:10 v/v): δ 164.29, 158.23, 156.23, 156.10, 149.48, 142.51, 142.39, 134.66, 131.84, 128.46, 127.89, 127.18, 126.78, 120.90, 119.89, 119.33, 115.99, 115.95, 114.78, 114.45, 64.76, 16.20, 15.03. MS (ESI, MeOH): *m*/*z* 453.1 $(M + Na)^+$, 883.2 $(2\ M + Na)^+$. Anal. calcd for $C_{23}H_{20}N_2O_3Ni$: C, 64.08; H, 4.68; N, 6.50. Found: C, 64.00; H, 4.64; N, 6.40.

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Supporting Information Available: Relevant spectroscopic data and copies of spectra and crystallographic data in CIF format. This material is free of charge via the Internet at http://pubs.acs.org.

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