DOI: 10.1002/ejic.200800274

A Modular Approach Towards Nonsymmetrical Bis(metallosalen) Building Blocks

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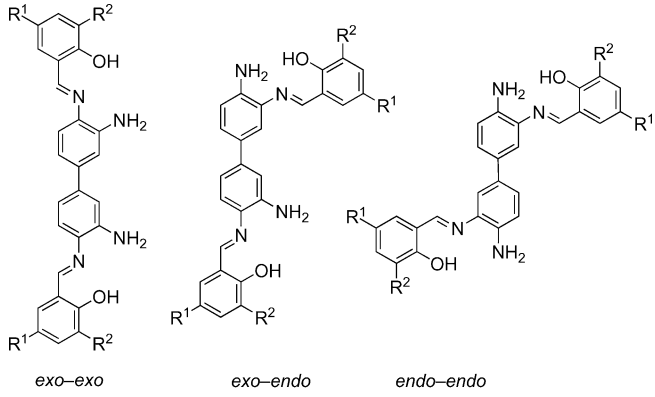
Keywords: N,O ligands / Salen ligands/ Zinc / Supramolecular chemistry

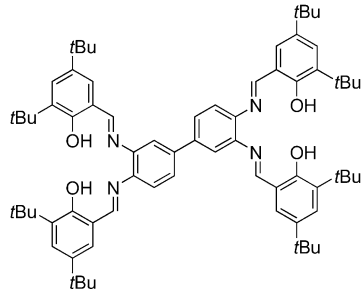
New bis(metallosalen) building blocks are described that can be accessed through di- or tetraimine precursors derived from the 3,3′-diaminobenzidine backbone. A selective procedure for the introduction of two imine groups in 3,3′-diaminobenzidine was developed to furnish starting materials for nonsymmetrical metallosalen complexes. The procedure proved to be widely applicable and several diimine derivatives were isolated and fully characterized. The diimine compounds were used to prepare the first nonsymmetrical bis(salen) complexes (M = Zn, Ni) with different peripheral groups upon treatment with various salicylaldehydes in a one-pot procedure. The identity of the bis(metallosalen)s was verified by a range of analytical techniques, and for two of these derivatives the X-ray molecular structures are described. The crystallographic data revealed that the biphenylene linker between the two N_2O_2 donor sets can adopt conformations with different dihedral angles. The supramolecular potential of the bis[Zn(salen)] derivatives was investigated by combining two of these complexes with a ditopic ligand to yield supramolecular assemblies with nanoscale dimensions.

Introduction

Salen ligands play a profound role in the development of catalytic procedures for a number of organic transformations[1] such as asymmetric conjugate additions,[2] (ep)-oxidation reactions[1i,3] and cyclopropanation.[4] In most known cases, the designed salen structure has a symmetrical character and is easily accessed by well-known preparative routes.[5] Recently, the attention has increasingly shifted to the construction of nonsymmetrical versions of salen ligands,[6] as the structural asymmetry is believed to allow better control over the catalytic properties of the ligated metal. The introduction of different substituents through the diamine or salicylaldehyde precursor provides a method to simultaneously control the steric crowding around the metal centre, as well as the electronic properties. For instance, improved enantioselectivities in various reactions may be achieved with nonsymmetrical salens as opposed to their symmetrical analogues.[7] Another benefit from the dissymmetry in the salen structure is a more-versatile approach towards immobilization of salen catalysts on a support through a single connection, thereby retaining catalyst systems with accessible and reactive sites.[8] Additionally,



1: $R^1 = R^2 = t$Bu
2: $R^1 = H$; $R^2 = t$Bu
3: $R^1 = R^2 = H$



Scheme 1. Isomeric diimines **1**–**3** and a (symmetrical) tetraimine compound based on the 3,3′-diaminobenzidine skeleton.

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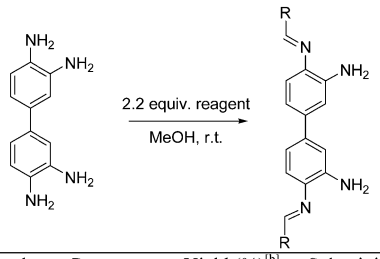
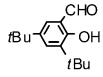
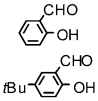
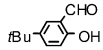
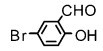
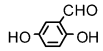
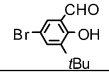
Table 1. Formation of diimine precursors **1**–**9** upon treatment of 3,3′-diaminobenzidine with various salicylaldehydes (R-CHO).[a] For simplicity, only the *exo–exo* isomer is shown above.



Compound	Reagent	Yield (%)[b]	Selectivity (%)[c]
1		90 (24)	51
2		89 (47)	92
3		87 (86)	≥98
4		72	80
5		92	48
6		73	≥95
7		86	50
8		79	40
9		67 (24)	50

[a] General conditions: MeOH, r.t., aldehyde (2.2 equiv.), 16–18 h. [b] Isolated yield of the isomeric diimine mixtures; yield of the *exo–exo* isomer after crystallization is in parentheses. [c] Selectivity for the *exo–exo* isomer was determined by ^{1}H NMR signal integration in the OH region.

the presence of two separate N,O-chelating salicylideneimine groups can provide access to interesting push–pull systems.[9] We recently communicated a versatile approach towards new di- and tetraimine ligands based on 3,3′-diaminobenzidine and commercially available salicylaldehydes (Scheme 1, cf. **1**, **2**).[10] These diimine precursors provided a useful platform for the construction of new nonsymmetrical, bimetallic bis(salphen) [salphen = *N*,*N*′-bis(salicylidene)-1,2-diaminobenzene] complexes. These sal(ph)en complexes are currently of great interest in the field of supramolecular chemistry and material science[11] and have shown in some cases an unusual reactivity behaviour.[12] Alternatively, the construction of bimetallic salen complexes may find their use in homogeneous catalysis as (cooperative) bimetallic activators[13] of (lethargic) substrates depending on the intermetal distance.

Here, we describe a modular approach for the synthesis of nonsymmetrical[14] bimetallic salphen complexes with an ample scope. The stepwise construction starts with the isolation of various diimine precursors (Scheme 1), which are subsequently converted into bimetallic species upon treatment with a range of different salicylaldehydes and metal salts to afford nonsymmetrical bis(metallosalphen) complexes that comprise different peripheral functional groups. These reactive groups may be useful as anchoring points or as an electronic tool to vary the properties of the metal centre. The X-ray molecular structures of two bis(metallosalphen) derivatives are reported, in which the benzidine scaffold shows conformational flexibility. The utility of these bimetallic building blocks is additionally demonstrated in the formation of supramolecular assemblies.

Results and Discussion

Synthesis of the Diimine (Ligand) Precursors

Our approach is based on the selective introduction of two or four imine groups in the 3,3′-diaminobenzidine skeleton.[10] The isolation of diimine derivatives can be readily achieved by using suitable reaction conditions, and crystallization of the crude materials may yield single diimine precursors (Table 1). Treatment of 3,3′-diaminobenzidine with either 3,5-di-*tert*-butylsalicylaldehyde, 3-di-*tert*-butylsalicylaldehyde or salicylaldehyde in MeOH at ambient temperature produced the desired diimine species **1**–**3**,[10] respectively, in high isolated yields as mixtures of geometrical isomers (Scheme 1). The products were isolated as yellow solids by filtration and dried, and the simple procedure enables the preparation of large amounts of materials (1–10 g). Remarkably, in the case of **2** and **3**, the crude reaction products nearly contained a single diimine isomer (see Figure 1 for comparison), whereas for the reaction that involved 3,5-di-*tert*-butylsalicylaldehyde, a mixture of three diimine isomers was isolated. The identity of the three isomeric struc-

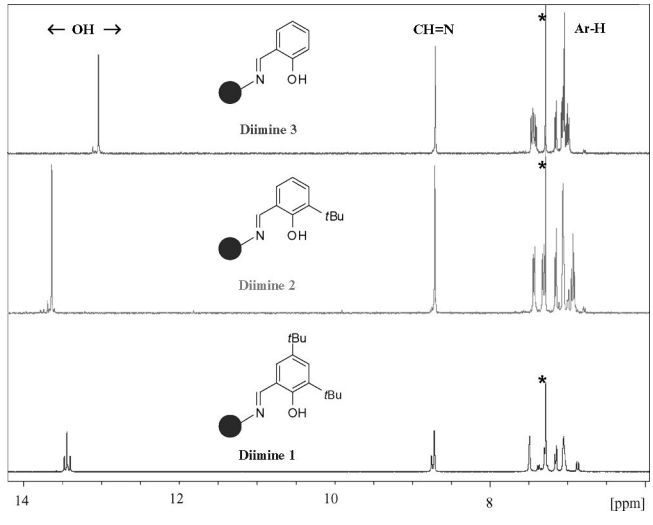


Figure 1. Selected NMR region ($CDCl_3$) for crude diimine species **1**–**3**. The asterisks denote the solvent residual signals. The dot schematically represents the 3,3′-diaminobenzidine backbone.

tures could be deduced from the OH region and comparison with two authentic samples of **1**-(*exo–exo*) and **1**-(*exo–endo*).[10]

The identity of diimine species **1**–**3** was initially corroborated by NMR spectroscopy and mass spectrometric techniques. ESI mass spectrometry revealed the exclusive presence of diimine structures in crude product **1**. Whereas diimine derivatives **2** and **3** were pure enough for further synthesis, recrystallization of crude **1** afforded a single diimine species (24% overall yield) based on 3,3′-diaminobenzidine. The sole presence of pure diimine compounds was easily recognized in the ^{1}H NMR spectra as a result of the presence of single peaks for the OH, imine and NH_2 groups in a 1:1:2 signal integral ratio. Definite proof of the structure of **1** and **2** was in both cases provided by X-ray crystallography (see Figure 2 for an example).[10] From the structure it is clear that a the symmetrical[15] *exo–exo* isomer was preferentially isolated by crystallization. Comparison of the NMR spectroscopic data of the crystalline samples obtained for these single isomers of **1** and **2** with crude products **1**–**3** authenticated the selective precipitation of similar *exo–exo* structures under the experimental conditions.

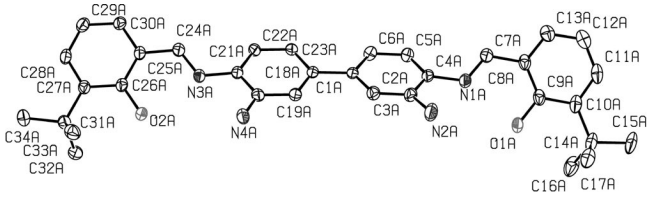


Figure 2. X-ray molecular structure determined for diimine compound **2** (*exo–exo* isomer). Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Only one of the crystallographic independent molecules in the unit cell is shown.

We then investigated the scope of this reaction in order to see whether the selective isolation of other useful diimine precursors could also be accomplished. For comparative reasons all experiments were conducted with one standard protocol (as reported for **1**–**3**, see Experimental Section) and the results are gathered in Table 1. Salicylaldehydes substituted with both apolar and polar groups were used. Generally, the isolated yields of diimine products are typically high, whereas the selectivity for the *exo–exo* isomer ranges from 40–98%. The latter seems to be a function of both the polarity and position of the peripheral groups. Although not reported here in much detail, several attempts were done with salicylaldehydes having other relatively polar groups (viz., the 3-ethoxy, 3-bromo, 5-iodo, 3,5-dinitro, 3-nitro and 3,5-dichloro derivatives), but because of the very low solubility characteristics of the isolated products no reliable assessment of the selectivity for diimine species could be carried out.

In these latter examples, NMR spectroscopic analysis was carried out in [D_6]dmso, which showed multiple species. Mass spectrometric analysis was additionally performed and proved to be in line with the NMR spectroscopic data: the presence of several species including mono- and triimines. The imine bond formation is potentially reversible under appropriate conditions and can thus lead to undesired exchange reactions between in situ aldimine groups and unreacted primary amines. The general observation of triimine and in certain cases even (traces of) tetraimine products with a low-solubility profile highly disfavours the clean isolation of diimine precursors, unlike that observed for diimines **1**–**9**.

Next, we examined the reaction of various (benz)aldehydes with 3,3′-diaminobenzidine in order to see if selective diimine formation would also be amenable to other reagents. The results of these studies are collected in Table 2. As observed for the diimine species presented in Table 1, the reaction of substituted (benz)aldehydes with 3,3′-diaminobenzidine selectively proceeds with remarkably high selectivity (90–98%) for the *exo–exo* isomer with isolated yields being moderate to high under these experimental conditions. The reason for the much lower *exo–exo* selectivity for the salicylaldehyde reagents (Table 1) may be ascribed to the presence of additional OH groups, which enforce different crystallization properties for the diimine species.

Table 2. Formation of diimine compounds **10**–**19** upon treatment of 3,3′-diaminobenzidine with various benzaldehydes (R-CHO).[a] For the schematic structure of the diimine species, see the figure accompanying Table 1.

Compound	Reagent	Yield (%)[b]	Selectivity (%)[c]
10		46	≥98
11		61	≥95
12		78	≥98
13		62	≥98
14		40	≥98
15		62	≥98
16		86	96
17		72	≥95
18		61	≥95
19		47	90

[a] General conditions: MeOH, r.t., aldehyde (2.2 equiv.), 16–18 h. [b] Isolated yield. [c] Selectivity for the *exo–exo* isomer was determined by ^{1}H NMR signal integration in the aromatic region.

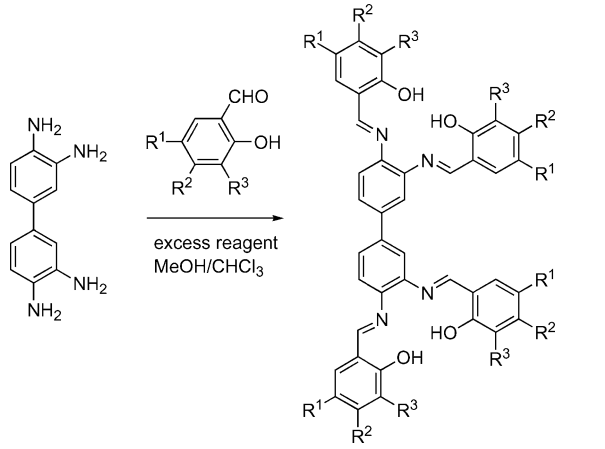
Subtle changes in the position of the aldehyde group on the aromatic ring may have a dramatic effect on the outcome of the reaction; for instance, the use of 1-naphthaldehyde as reagent (not reported here) reveals a compli-

cated mixture of components in the product after isolationas evidenced by NMR spectroscopic analysis, whereas the use of 2-naphthaldehyde gives rise to clean and selective diimine formation (Table 2, compound **16**). The reported isolated yields will probably be a function of the experimental conditions such as concentration and type of solvent; hence, they should be considered as nonoptimized.

Syntheses of Tetraimine Precursors

A series of tetraimine precursors could also be conveniently prepared by treatment of 3,3′-diaminobenzidine with an excess amount of the appropriate salicylaldehyde (5 equiv.) in a mixture of $CHCl_3$ and MeOH at ambient temperature (Table 3). The use of a co-solvent was necessary to prevent precipitation of the di- and triimine intermediate species. The clean formation of the tetraimine precursors was easily deduced from the NMR spectroscopic data, since all compounds show two separate peaks for the phenolic and imine protons with the expected signal integration ratio as compared to various other protons. Tetraimine **21** further reveals the presence of four distinct peaks for the *t*Bu groups in the ^1H NMR spectrum, while for **22** and **24** two separate signals are observed for the *t*Bu and Me groups, respectively. This corroborates with the fact that each salen unit in these tetraimines can be regarded as nonsymmetrical due to the presence of the 4-substitution in the bridging phenyl group. As for the proton NMR spectra, similar features were encountered in the $^{13}C\{^1H\}$ NMR spectra, e.g. two distinct imine-*C* were observed. The structures of the tetraimines **20**–**24** were fully supported by NMR, MS and elemental analyses. Some of these tetraimine precursors (**20** and **21**) were used for the preparation of symmetrical bimetallic salen complexes (see below).

Table 3. Formation of tetraimine precursors **20**–**24** upon treatment of 3,3′-diaminobenzidine with an excess amount of various salicylaldehydes.[a]

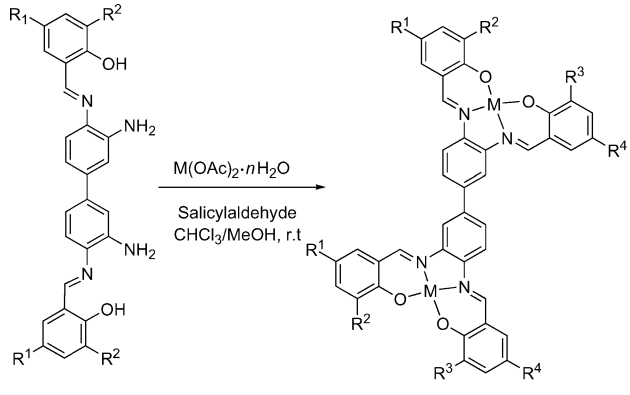


Compound	R^1	R^2	R^3	Yield [%][b]
20	H	H	H	91
21	*t*Bu	H	*t*Bu	64
22	*t*Bu	H	H	52
23	H	H	$-CH_2CH{=}CH_2$	72
24	H	H	Me	56

[a] General conditions: MeOH/$CHCl_3$, r.t., 16–18 h. [b] Isolated yield.

Synthesis of (Non)Symmetrical Bis(metallosalphen) Complexes

A selection of diimines **1**–**3** and tetraimines **20**–**24** were used as starting materials for the selective preparation of different (non)symmetrical, bimetallic salphen complexes **25**–**34** (Scheme 2). The general procedure comprises the combination of a 1:2 ratio between the diimine and metal precursor in the presence of 2 equiv. (or slight excess) of a different salicylaldehyde in $CHCl_3$/MeOH. Initially, a yellow solution is observed, which, depending on the respective product, is converted into a more intensively coloured suspension. Isolation of the pure products was generally achieved by concentration and trituration of the crude product with MeOH, or simply by filtration. Complexes **25**–**36** were fully characterized by using NMR spectroscopy, MALDI-TOF mass spectrometry and elemental analyses. For two of these complexes, the single-crystal X-ray molecular structures were determined (see below). The mass spectrum for any of the bis[Zn(salphen)] complexes **25**–**34** displays a characteristic isotope pattern for the M^+ ion, which allows fast identification (Figure 3). The nonsymmetry within each salen unit is easily recognized by the presence of two distinct imine protons in the NMR spectra, a feature that was also previously reported for related mononuclear systems.[6a]



1: $R^1 = R^2 = t$Bu
2: R^1 = H, $R^2 = t$Bu
3: $R^1 = R^2$ = H

25: $R^1 = R^2 = R^3 = R^4$ = H; M = Zn
26: R^1 = H, $R^2 = t$Bu, $R^3 = R^4 = NO_2$; M = Zn
27: R^1 = H, $R^2 = t$Bu, $R^3 = NO_2$, R^4 = H; M = Zn
28: R^1 = H, $R^2 = t$Bu, $R^3 = R^4$ = Cl; M = Zn
29: $R^1 = R^4$ = H, $R^2 = R^3 = NO_2$; M = Zn
30: $R^1 = R^2 = t$Bu, $R^3 = R^4 = NO_2$; M = Zn
31: $R^1 = R^2 = t$Bu; $R^3 = R^4$ = Cl
32: $R^1 = R^2 = R^3 = R^4 = t$Bu; M = Zn
33: $R^1 = R^2 = R^3 = R^4 = t$Bu; M = Ni
34: R^1 = H, $R^2 = t$Bu, R^3 = H, $R^4 = C_2$TMS; M = Zn

Scheme 2. Synthesis of nonsymmetric bimetallic salphen complexes **25**–**34**.

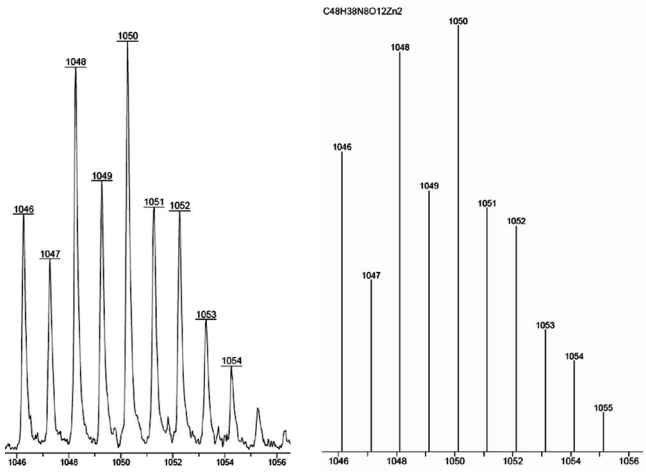


Figure 3. Observed $[M]^+$ and simulated mass spectra (at the right) for bis[Zn(salphen)] complex **26** ($C_{48}H_{38}N_8O_{12}Zn_2$) showing a diagnostic isotopic pattern.

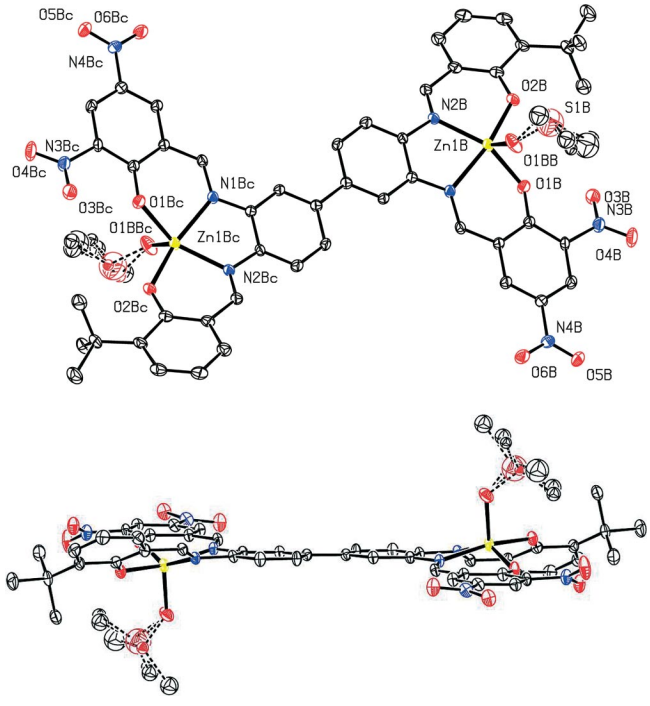


Figure 4. X-ray molecular structure for complex **26** with the adopted numbering scheme and showing disorder in the coordinating dmso ligands. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity and only one of the crystallographically independent molecules is shown (top). A side view of the molecule showing the flat nature of the biphenylene unit (bottom). Selected interatomic distances [Å] and angles [°] with estimated standard deviations in parentheses: Zn1B–N1B 2.106(2), Zn1B–N2B 2.045(3), Zn1B–O1B 2.003(2), Zn1B–O2B 1.9629(19), Zn1B–O1BB 2.018(2), O1BB–Zn1B–O1B 96.00(10), O1BB–Zn1B–O2B 101.89(9), O1B–Zn1B–O2B 96.61(8), O1B–Zn1B–N1B 87.57(9), O1B–Zn1B–N2B 144.16(9), O2B–Zn1B–N1B 165.36(9), O2B–Zn1B–N2B 90.06(8), N1B–Zn1B–N2B 78.56(9), C9B–C10B–C10Bc–C9Bc 180.0(3), C11B–C10B–C10Bc–C11Bc –180.0(3).

X-ray Structural Analysis of Bimetallic Complexes

Crystals of compounds **26** and **30** suitable for X-ray diffraction were obtained by heating a dmso solution of the respective compound and then cooling the clear solution to ambient temperature, slowly after which orange-to-red needle-shaped crystals deposited. The molecular structures were determined and are presented in Figures 4 and 5.[16,17]

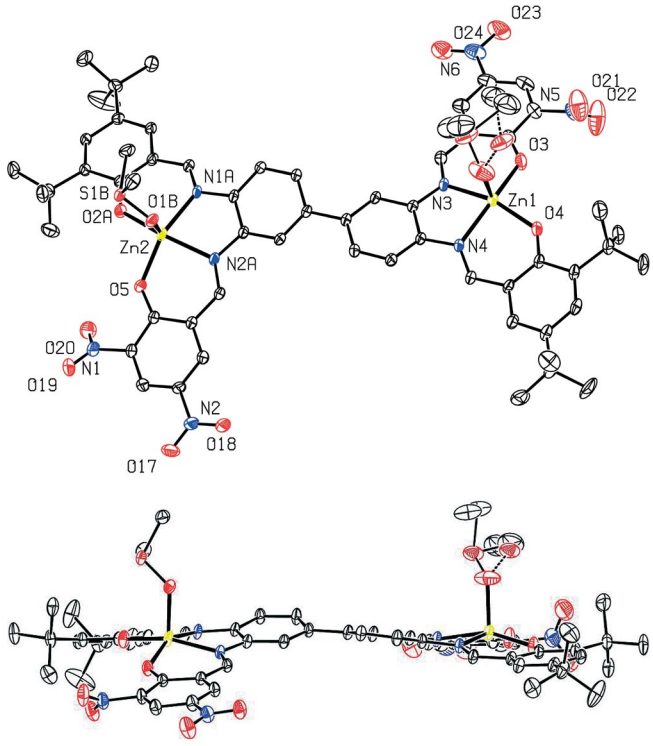


Figure 5. X-ray molecular structure of compound **30** with the adopted numbering scheme and showing some disorder in one of the coordinating dmso molecules. Hydrogen atoms, cocrystallized solvent molecules and numbering scheme are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn1–N3 2.116(3), Zn1–N4 2.059(4), Zn1–O3 2.006(4), Zn1–O4 1.946(3), Zn1–O1D 2.022(5), O1D–Zn1–O3 101.6(2), O1D–Zn1–O4 103.90(19), O3–Zn1–O4 94.69(13), O3–Zn1–N3 88.39(14), O3–Zn1–N4 157.22(15), O4–Zn1–N3 157.19(15), O4–Zn1–N4 90.70(13), N3–Zn1–N4 78.45(14), C18A–C19A–C31–C32 157.3(5), C20A–C19A–C31–C30 156.0(5).

Bis(Zn^{II}) compound **26** exists as a bis(dmso) complex in the solid state, in which both dmso ligands occupy *anti* positions with respect to the bis(salphen) plane. The coordination of dmso to the Zn centre renders the geometry around these metal ions approximately square pyramidal. Both Zn centres are lifted from the N_2O_2 ligand pocket, in which one of the oxygen atoms is significantly displaced from the basal plane. Another feature worth pointing out is the nearly flat nature of the biphenyl fragment within **26** (dihedral angle ca. 0°). This is in sharp contrast with the molecular structure determined for **30**, in which the same biphenyl fragment shows a torsion angle of around 23–24°. In the latter structure, the unit cell comprises the presence of two, crystallographically independent molecules that have two axial dmso ligands residing at the same side of the

bis(salphen) plane. This feature is probably a consequence of maximizing the packing efficiency. The voids within the crystal lattices of **26** and **30** are filled with multiple disordered dmso molecules.

Formation of Supramolecular Assemblies

Bimetallic Zn complex **31** was used as a building block for the construction of a supramolecular assembly by combination of **31** (1 equiv.) with 4,4′-dipyridine (bipy; 1 equiv.). Crystalline material was obtained from a (concentrated) dmso solution, and the crystals were evaluated by X-ray analysis.[18] Remarkably, in the determined structure, the axial position is occupied by the pyridine donor and no axial ligation of dmso was observed. The structure can best be described as a 2D-polymeric ladder-type assembly (Figures 6 and 7), of which the individual sheets line up to form a 3D network. The Zn–N_{pyr} distance in assembly **31**·bipy is 2.083 Å, which is closely related to a number of comparable Zn(salphen) structures based on this coordination motif.[6a,19] As a result of the very low solubility features of **31**·bipy, the ^{1}H NMR spectrum was recorded in [D_6]dmso. The bipy resonances showed, as expected, no signal displacement under these conditions. This result is in line with the coordination of (bulk) dmso and no assembly formation is therefore expected in dmso solution. Because other solvents failed to solubilize assembly **31**·bipy, the potential assembly formation in solution was further studied in [D_8]thf.

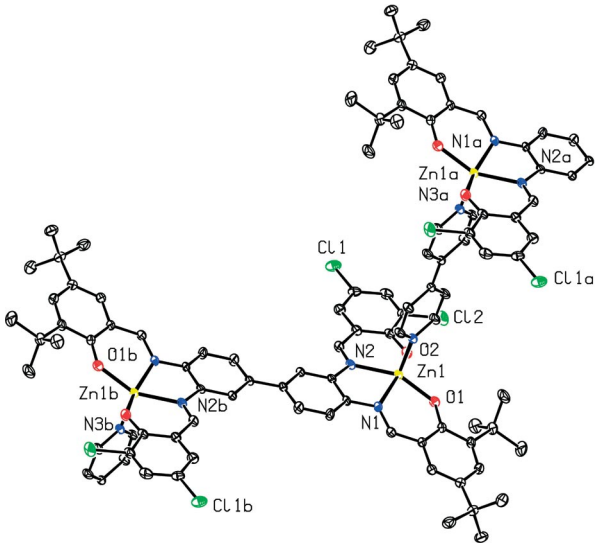


Figure 6. The repeating unit of (**31**·bipy)$_n$ with accompanying numbering scheme is shown. Hydrogen atoms and cocrystallized solvent molecules are omitted for clarity. Selected interatomic distances [Å] and angles [°]: Zn1–N1 2.058(3), Zn1–N2 2.131(3), Zn1–N3 2.083(3), Zn1–O1 1.955(2), Zn1–O2 1.969(3), O1–Zn1–O2 93.03(11), O1–Zn1–N1 90.30(11), O1–Zn1–N2 151.98(10), O1–Zn1–N3 105.91(9), O2–Zn1–N1 156.89(10), O2–Zn1–N2 88.60(11), O2–Zn1–N3 95.46(11), N1–Zn1–N2 78.03(10), N1–Zn1–N3 105.60(11), N2–Zn1–N3 101.76(10).

The ^{1}H NMR spectrum recorded in [D_8]thf for the 1:1 combination of **31** and bipy showed a modest *upfield* shift for the pyridine–H_{ortho} of –0.06 ppm, which indicates some

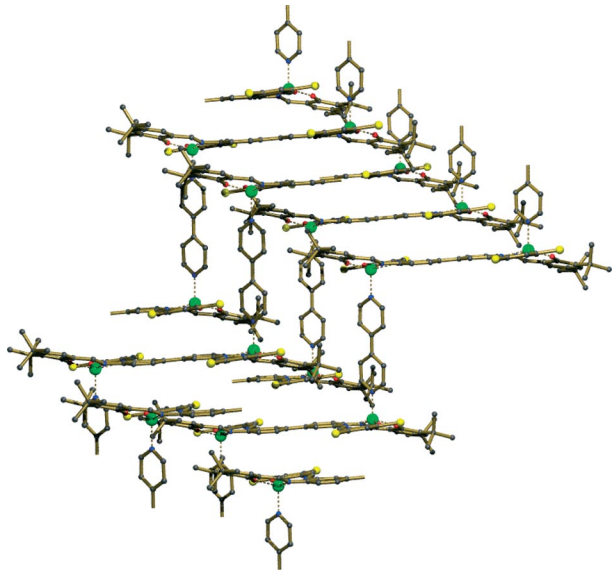


Figure 7. Part of the packing diagram for polymeric assembly (**31**·bipy)$_n$. Colour codes: Zn = green, O = red, N = blue, Cl = yellow, C = grey.

degree of pyridine binding at the Zn metal centre. The solution structure was then further investigated by ^{1}H diffusion ordered spectroscopy (DOSY, see Supporting Information). The ^{1}H DOSY NMR spectrum (with complex **31** at ca. 1 mM) did not display a single species as was evident from the different diffusion coefficients for the complex and the 4,4′-bipyridine components, from which we conclude that no discrete assembly is present under these conditions, but a rapid exchange between several small (oligomeric) species probably occurs as a result of the dynamic nature of the Zn–N_{pyr} coordinative bond. Furthermore, complex **32** was also combined with 4,4′-bipyridine (1:1 molar ratio) in [D_6]acetone, and an upfield shift of –0.12 ppm was noted for the H_{ortho} of the pyridine donor, which is consistent with assembly formation and with slower Zn–N_{pyr} dynamics relative to the assembly formation in [D_8]thf. The ^{1}H DOSY NMR, however, indicated as for **31**·bipy (Supporting Information) the presence of a dynamic mixture of components.

Conclusions

We here present a general approach towards nonsymmetrical, bimetallic salen derivatives. The reported stepwise route utilizes valuable diimine precursors that can be easily derived from commercially available 3,3′-diaminobenzidine in good yields. In general, the isolated yields for the nonsymmetric bimetallic structures are also high, and simple procedures were developed that allow the introduction of various functional groups. These groups are important, as they vary the physical properties (solubility, tendency towards dimerization in the case where M = Zn and Lewis acidity of the metal ions) of these building blocks. Although the present studies are narrow in scope with respect to the type of metal ions present in the bis(salen) scaffolds (M = Zn, Ni), we believe that this can be easily extended to vari-

ous other (paramagnetic) metal ions in order to arrive at structures relevant for homogeneous catalysis applications.[12a] X-ray analyses of two of these bimetallic synthons have shown that the structure of the biphenyl subunit is flexible, which allows flattened or slightly bent molecules. The potential application of these bimetallic salphen derivatives was demonstrated by the formation of a supramolecular assembly combining bimetallic building blocks **31** and **32** with a suitable ditopic ligand. Other applications are foreseen in homogeneous catalysis by using the bimetallic structures in efficient catalytic operations that require bimetallic activation or cooperativity.[2] Furthermore, once heterobimetallic structures can be accessed, an intelligent combination of two different metal ions may lead to multistep process chemistry, in which each of the metal ions exerts a specific conversion/interaction. Our focus in this area will optimistically lead to new developments in homogeneous catalysis based on salen technology.

Experimental Section

General: The syntheses of diimines **1** and **2**,[10] tetraimines **20**[20] and **21**,[10] complexes **27**, **28**, **32** and **33**,[10] 5-trimethylsilylacetylylsalicylaldehyde[21] and 5-bromo-3-*tert*-butylsalicylaldehyde[22] are described elsewhere. All reagents were commercially purchased and used without further purification. Mass spectrometric measurements were carried out at the ICIQ mass spectrometric facility. Elemental analyses were obtained from the Unidad de Análisis Elemental, Universidad de Santiago de Compostela (Spain). All NMR measurements were carried out with Bruker 400 MHz spectrometers and chemical shifts are referenced to internal TMS.

Standard Protocol for the Syntheses of Diimine Compounds: A mixture of 3,3′-diaminobenzidine (typically 0.20–0.50 g, 0.9–2.3 mmol) was suspended in MeOH (50 mL), and subsequently the appropriate salicylaldehyde (2.2 equiv.) was added as a solution in MeOH (5–10 mL). The yellow/orange reaction mixture was then stirred for 18 h, and the product was collected by filtration and dried following analysis.

Diimine 3: Yellow solid, yield 87% after recrystallization from hot acetone. The crude product was close to pure. ^{1}H NMR (400 MHz, [D$_6$]acetone): δ = 13.08 (s, 2 H, OH), 8.91 (s, 2 H, CH=N), 7.63 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 2 H, ArH), 7.43 (m, 2 H, ArH), 7.28 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.19 (d, ^4J = 2.0 Hz, 2 H, ArH), 7.00 (m, 6 H, ArH), 4.90 (s, 4 H, NH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]dmso): δ = 160.21, 159.81, 143.02, 139.76, 133.48, 132.72, 131.97, 120.08, 119.09, 118.66, 116.44, 115.08, 113.04 ppm. MS (ESI): *m*/z = 445.4 [M + Na]$^+$. $C_{26}H_{22}N_4O_2$ (422.48): calcd. C 73.92, H 5.25, N 13.26; found C 73.51, H 5.38, N 13.29.

Diimine 4: Yellow solid, yield 72%. Mixture of three isomers in a 80:12:8 ratio. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 12.89 (s, 1 H, OH, minor), 12.86 (s, 1 H, OH, minor), 12.83 (s, 2 H, OH, major), 12.800 (s, 1 H, OH, minor), 12.795 (s, 1 H, minor), 8.76 (s, 1 H, CH=N, minor), 8.742 (s, 1 H, CH=N, minor), 8.739 (s, 1 H, CH=N, minor), 8.73 (s, 1 H, CH=N, minor), 8.72 (s, 1 H, CH=N, minor), 8.71 (s, 2 H, CH=N), 7.47 (d, ^3J = 8.6 Hz, ^4J = 2.5 Hz, 2 H, ArH, major), 7.43 (d, ^4J = 2.4 Hz, 2 H, ArH, major), 7.15 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.04 (d, ^3J = 8.6 Hz, ^4J = 1.9 Hz, 2 H, ArH, major), 7.04 (s, 2 H, ArH, major), 7.01 (d, ^3J = 8.6 Hz, 2 H, ArH, major), 4.11 (s, 4 H, NH$_2$, major), 1.37 [s, 18 H, C(CH$_3$)$_3$, major] ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 162.5, 158.9, 142.4, 141.4, 140.9, 135.1, 130.9, 129.0, 119.2, 118.9, 117.9, 117.0, 114.4, 34.4, 31.8 ppm. MS (ESI): *m*/*z* = 557.3 [M + Na]$^+$, 535.3 [M + H]$^+$. $C_{34}H_{38}N_4O_2$ (534.69): calcd. C 76.37, H 7.16, N 10.48; found C 76.13, H 7.05, N 9.81.

Diimine 5: Orange solid, yield 92%. Mixture of three isomers in a 48:46:6 ratio. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 13.10 (s, 1 H, OH, major), 13.06 (s, 2 H, OH, major), 13.04 (s, 2 H, OH, minor), 13.01 (s, 1 H, OH, major), 8.66 (s, 1 H, CH=N, major), 8.65 (s, 2 H, CH=N, minor), 8.62 (br., 1 H, 2 H, CH=N, 2× major), 7.58 (d, ^4J = 2.4 Hz, 1 H, ArH, major), 7.57 (d, ^4J = 2.4 Hz, 2 H, ArH, major), 7.55 (d, ^4J = 2.3 Hz, 2 H, ArH, minor), 7.51 (d, *J* not resolved, 1 H, ArH, major), 7.50 (d, ^4J = 2.5 Hz, 2 H, ArH, major), 7.49 (d, *J* not resolved, 1 H, ArH, major), 7.48 (d, ^4J = 2.6 Hz, 2 H, ArH, major), 7.47 (d, *J* not resolved, 1 H, ArH, major), 7.41 (d, ^4J = 2.0 Hz, 1 H, ArH, major), 7.27 (d, ^4J = 2.0 Hz, 1 H, ArH, major), 7.15 (s, 1 H, ArH, major), 7.13 (s, 1 H, ArH, major), 7.06 (d, ^4J = 1.9 Hz, 1 H, ArH, major), 7.04 (s, 2 H, ArH, major), 7.01 (br., ArH, major), 6.98 (pseudo t, ^4J = 2.3 Hz, 2 H, ArH, major), 6.96 (pseudo t, ^4J = 2.3 Hz, 2 H, ArH, major), 6.89 (s, 1 H, ArH, major), 6.87 (s, 1 H, ArH, major), 4.12 (br., 4 H, NH$_2$, 2× major), 4.06 (s, 4 H, NH$_2$, minor) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]-dmso): δ = 159.24, 158.91, 158.80, 158.75, 158.58, 157.75, 157.17, 156.80, 143.43, 143.40, 143.31, 142.63, 141.53, 141.49, 141.25, 141.10, 140.13, 140.05, 135.18, 135.07, 135.03, 134.97, 134.90, 134.85, 134.69, 134.58, 134.30, 134.27, 134.02, 133.57, 133.37, 133.27, 133.17, 132.21, 131.63, 129.12, 129.06, 128.53, 126.12, 125.69, 125.54, 122.26, 122.18, 122.04, 119.17, 118.87, 118.84, 118.81, 118.59, 118.43, 118.25, 117.46, 116.61, 116.12, 115.86, 115.67, 115.54, 115.20, 115.09, 114.88, 114.64, 114.53, 113.12, 112.43, 112.37, 112.12, 110.09, 110.06, 110.04, 110.01, 109.95, 109.88 (all Ar-C) ppm. MS (ESI): *m*/*z* = 581.0 [M + H]$^+$, 603.0 [M + Na]$^+$. $C_{26}H_{20}Br_2N_4O_2$·1/3H$_2$O (586.27): calcd. C 53.26, H 3.55, N 9.56; found C 53.30, H 3.09, N 9.43.

Diimine 6: Yellow solid, yield 73%. ^{1}H NMR (400 MHz, [D$_6$]-dmso): δ = 11.96 (s, 2 H, OH), 9.07 (s, 2 H, OH), 8.81 (s, 2 H, CH=N), 7.22 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.08 (d, ^4J = 2.8 Hz, 2 H, ArH), 7.04 (d, ^4J = 1.8 Hz, 2 H, ArH), 6.79–6.88 (m, 4 H, ArH), 6.81 (s, 2 H, ArH), 5.15 (s, 4 H, NH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 162.5, 158.9, 142.4, 141.4, 140.9, 135.1, 130.9, 129.0, 119.2, 118.9, 117.9, 117.0, 114.4, 34.4, 31.8 ppm. MS (ESI): *m*/*z* = 455.1 [M + H]$^+$. $C_{34}H_{38}N_4O_2$ (454.48): calcd. C 76.37, H 7.16, N 10.48; found C 76.13, H 7.05, N 9.81.

Diimine 7: Yellow solid, yield 86%. Mixture of two isomers in a 50:50 ratio. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 13.32 (s, 1 H, OH), 13.28 (s, 2 H, OH), 13.24 (s, 1 H, OH) 8.73 (s, 1 H, CH=N, one isomer), 8.693 (s, 2 H, CH=N, one isomer) 8.689 (s, 1 H, CH=N, one isomer), 7.38 (d, ^4J = 2.0 Hz, ^3J = 8.2 Hz, ArH), 7.00–7.07 (m, ArH, both isomers) 6.85–6.94 (m, ArH, both isomers), 4.13 (s, 4 H, NH$_2$, both isomers), 1.57 (s, 6 H, CH$_3$, both isomers) ppm. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ = 163.0, 162.2, 161.8, 159.43, 159.41, 153.38, 141.6, 141.4, 141.1, 141.0, 140.7, 136.0, 135.0, 34.6, 134.5, 134.4, 134.3, 131.9, 130.4, 130.3, 130.2, 126.8, 126.5, 126.4, 119.2, 119.18, 119.15, 119.09, 118.92, 118.90, 118.0, 117.4, 117.2, 116.3, 114.4, 114.0 ppm. MS (ESI): *m*/*z* = 451.2 [M + H]$^+$, 473.2 [M + Na]$^+$. $C_{28}H_{26}N_4O_2$ (450.53): calcd. C 74.65, H 5.82, N 12.44; found C 74.40, H 5.76, N 12.44.

Diimine 8: Orange solid, yield 79%. Mixture of three isomers in a 39:45:16 ratio. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 13.36 (s, 1 H, OH, major), 13.31 (s, 2 H, OH, major), 13.30 (s, 2 H, OH, minor), 13.28 (s, 1 H, OH, major), 8.731 (s, 1 H, CH=N, major), 8.727 (s, 2 H, CH=N, minor), 8.701 (s, 2 H, CH=N, major), 8.697 (s, 1 H, CH=N, major), 7.39 (d, ^4J = 2.0 Hz, 1 H, ArH, major), 7.37 (d, ^4J = 2.0 Hz,

1 H, ArH, major), 7.29–7.36 (m, ArH, minor and major isomers), 7.24 (d, ^4J = 2.0 Hz, 1 H, ArH, major), 7.15 (d, ^3J = 8.8 Hz, 2 H, ArH, major), 7.057 (s, 1 H, ArH, minor), 7.053 (s, 1 H, ArH, major), 7.039 (s, 1 H, ArH, major), 7.035 (s, 2 H, ArH, major), 7.022 (s, 1 H, ArH, minor), 7.017 (s, 1 H, ArH, major), 6.92–6.98 (m, ArH, different isomers), 6.87 (d, ^3J = 8.2 Hz, 2 H, ArH, major), 6.05–6.15 (m, 1 H, CH_2-C*H*=CH_2, different isomers), 5.12–5.18 (m, 2 H, CH_2-CH=CH_2, different isomers), 4.13 (br. s, 4 H, NH_2, major isomers), 4.07 (s, 4 H, minor), 3.52 (d, ^3J = 6.5 Hz, CH_2-CH=CH_2, different isomers) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]-dmso): δ = 162.51, 162.33, 161.41, 160.68, 158.03, 158.00, 157.93, 157.90, 142.94, 142.17, 141.17, 139.91, 139.85, 136.57, 134.20, 133.16, 132.98, 132.88, 132.73, 132.17, 130.91, 130.80, 130.69, 129.35, 128.83, 127.11, 127.08, 127.05, 125.87, 125.45, 119.28, 119.24, 119.22, 118.85, 118.83, 118.78, 118.65, 116.43, 115.91, 115.87, 115.85, 115.78, 115.27, 114.87, 113.26, 112.63 (all ArC and allyl-C), 33.09 (-*C*-C=C) ppm. MS (ESI): *m*/*z* = 503.3 [M + H]$^+$, 525.2 [M + Na]$^+$. $C_{32}H_{30}N_4O_2 \cdot 1/3H_2O$ (508.61): calcd. C 75.57, H 6.08, N 11.02; found C 75.48, H 5.71, N 10.90.

Diimine 9: Yellow-to-orange solid, yield 67%. Mixture of three isomers in a 50:25:25 ratio. Recrystallization from warm $CHCl_3$ produced the pure *exo–exo* isomer (24% yield). ^1H NMR (400 MHz, $CDCl_3$): δ = 13.73 (s, 1 H, OH, minor), 13.70 (s, 2 H, OH, major), 13.68 (s, 2 H, OH, minor), 13.65 (s, 1 H, OH, minor), 8.66 (s, 1 H, CH=N, minor), 8.65 (s, 2 H, CH=N, minor), 8.62 (br. s, 2 H, 1 H, CH=N, major and minor), 7.34–7.49 (m, ArH, different isomers), 7.21 (d, ^4J = 1.9 Hz, 1 H, ArH, minor), 7.15 (s, 1 H, ArH, minor), 7.13 (s, 2 H, major), 7.02–7.07 (m, ArH, major and minor), 6.88 (d, ^3J = 8.2 Hz, 2 H, ArH, major), 4.15 (br. s, NH_2, major and minor isomer), 4.09 (br. s, NH_2, minor), 1.48 [br., $C(CH_3)_3$, major and minor] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 161.60, 160.67, 160.29, 159.38, 141.56, 141.42, 140.97, 140.79, 140.67, 140.41, 139.93, 135.20, 134.01, 133.36, 133.26, 133.15, 132.57, 132.48, 131.88, 131.46, 126.98, 126.59, 120.93, 120.86, 119.95, 118.66, 117.77, 117.27, 116.81, 116.55, 116.39, 114.33, 113.77, 110.65, 35.35, 29.34 ppm. MS (ESI): *m*/*z* = 693.1 [M + H]$^+$. $C_{34}H_{36}N_4O_2Br_2$ (692.48): calcd. C 58.97, H 5.24, N 8.09; found C 59.06, H 5.15, N 7.95.

Diimine 10: Yellow solid, yield 46%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.73 (s, 2 H, CH=N), 8.04–8.01 (m, 4 H, ArH), 7.51–7.53 (m, 6 H, ArH), 7.24 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.02 (d, ^4J = 1.9 Hz, 2 H, ArH), 6.84 (d, ^4J = 1.9, ^3J = 8.3 Hz, 2 H, ArH), 5.34 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 155.9, 144.3, 139.7, 136.7, 134.3, 130.9, 128.7, 128.6, 117.3, 114.5, 112.3 ppm. MS (ESI): *m*/*z* = 391.2 [M + H]$^+$, 413.2 [M + Na]$^+$. $C_{26}H_{22}N_4$ (390.48): calcd. C 79.97, H 5.68, N 14.35; found C 79.84, H 5.63, N 14.29.

Diimine 11: Orange solid, yield 61%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.90 (s, 2 H, OH), 8.61 (s, 2 H, CH=N), 7.89 (d, ^3J = 8.6 Hz, 4 H, ArH), 7.16 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.07 (d, ^4J = 1.9 Hz, 2 H, ArH), 6.97 (d, ^3J = 8.6 Hz, ^4J = 2.0 Hz, 4 H, ArH), 6.91 (d, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 2 H, ArH), 4.91 (br. s, NH_2) ppm. The product was too insoluble for a ^{13}C NMR measurement. MS (ESI): *m*/*z* = 445.1 [M + Na]$^+$. $C_{26}H_{22}N_4O_2 \cdot 0.8H_2O$ (436.89): calcd. C 71.48, H 5.44, N 12.82; found C 71.26, H 5.29, N 12.99.

Diimine 12: Yellow solid, yield 78%. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.99 (s, 2 H, CH=N), 7.12 (m, 6 H, ArH), 6.97 (s, 4 H, ArH), 4.29 (s, 4 H, NH_2), 2.61 (s, 12 H, CH_3), 2.35 (s, 6 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 158.9, 143.6, 139.5, 139.1, 138.3, 136.3, 130.4, 129.7, 117.3, 114.8, 112.2, 21.2, 20.8 ppm. MS (ESI): *m*/*z* = 475.3 [M + H]$^+$, 497.2 [M + Na]$^+$. $C_{32}H_{34}N_4 \cdot 1/3H_2O$ (480.64): calcd. C 79.96, H 7.27, N 11.60; found C 79.97, H 7.14, N 11.80.

Diimine 13: Yellow solid, yield 62%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.73 (s, 2 H, CH=N), 8.10 (d, ^4J = 2.0 Hz, ^3J = 7.8 Hz, 2 H, ArH), 8.09 (d, ^4J = 2.0 Hz, ^3J = 7.8 Hz, 2 H, ArH), 7.37 (d, ^4J = 1.8 Hz, ^3J = 8.8 Hz, 2 H, ArH), 7.35 (d, ^4J = 1.9 Hz, ^3J = 7.9 Hz, 2 H, ArH), 7.23 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.00 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.83 (dd, ^4J = 2.0 Hz, ^3J = 8.2 Hz, 2 H, ArH), 5.34 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 165.4, 162.9, 155.0, 144.8, 140.2, 134.6, 133.9 ($J_{C,F}$ = 2.8 Hz), 131.3 ($J_{C,F}$ = 8.7 Hz), 117.8, 116.3, 116.1, 114.9 ppm. MS (ESI): *m*/*z* = 427.1 [M + H]$^+$. $C_{26}H_{20}F_2N_4$ (426.46): calcd. C 73.23, H 4.73, N 13.14; found C 73.30, H 4.56, N 13.15.

Diimine 14: Yellow solid, yield 40%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.98 (s, 2 H, CH=N), 8.38 (d, ^4J = 1.9 Hz, ^3J = 7.6 Hz, 2 H, ArH), 7.60–7.47 (m, 6 H, ArH), 7.24 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.02 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.84 (d, ^4J = 2.0 Hz, ^3J = 8.2 Hz, 2 H, ArH), 5.44 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 151.1, 144.7, 140.3, 134.5, 134.1, 133.2, 132.2, 129.9, 128.8, 127.5, 117.4, 114.6, 112.4 ppm. MS (ESI): *m*/*z* = 459.1 [M + H]$^+$. $C_{26}H_{20}Cl_2N_4$ (459.37): calcd. C 67.98, H 4.39, N 12.20; found C 67.64, H 4.06, N 12.19.

Diimine 15: Yellow solid, yield 62%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.53 (s, 2 H, CH=N), 7.94 (d, ^4J = 1.2 Hz, 2 H, ArH), 7.19 (d, ^3J = 8.3 Hz, 2 H), 7.17 (d, ^4J = 3.4 Hz, 2H ArH), 6.99 (d, ^4J = 1.9 Hz, 2 H, ArH), 6.81 (d, ^4J = 1.9 Hz, ^3J = 8.2 Hz, 2 H, ArH), 6.73–6.71 (m, 2 H, ArH), 5.23 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 152.7, 145.9, 144.2, 144.1, 139.6, 134.3, 116.7, 115.5, 114.0, 112.4, 111.6 ppm. MS (ESI): *m*/*z* = 371.1 [M + H]$^+$, 393.1 [M + Na]$^+$. $C_{22}H_{20}N_4O_2$ (370.40): calcd. C 70.95, H 5.41, N 15.04; found C 70.73, H 4.75, N 15.25.

Diimine 16: Yellow solid, yield 86%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.42 (s, 2 H, CH=N), 8.31 (d, ^4J = 1.3 Hz, ^3J = 8.6 Hz, 2 H, ArH), 8.07–7.99 (m, 8 H, ArH), 7.64–7.60 (m, 4 H, ArH), 7.32 (d, ^3J = 8.3 Hz, 2 H), 7.04 (d, ^4J = 2.0 Hz, 2H ArH), 6.88 (d, ^4J = 1.9 Hz, ^3J = 8.2 Hz, 2 H, ArH), 5.42 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 155.6, 144.5, 139.8, 134.5, 134.9, 134.3, 132.8, 130.7, 128.6, 128.3, 127.8, 127.4, 126.7, 123.9, 117.3, 114.6, 112.4 ppm. MS (ESI): *m*/*z* = 491.2 [M + H]$^+$. $C_{34}H_{26}N_4$ (490.60): calcd. C 83.24, H 5.34, N 11.42; found C 83.08, H 5.12, N 11.41.

Diimine 17: Orange solid, yield 72%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 8.77 (s, 2 H, CH=N), 8.71 (d, ^3J = 5.9 Hz, 4 H, Pyr-H), 7.94 (d, ^3J = 6.0 Hz, 4 H, Pyr-H), 7.32 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.03 (d, ^4J = 1.8 Hz, 2 H, ArH), 6.84 (d, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 2 H, ArH), 5.52 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 153.40, 150.27, 145.16, 143.25, 140.67, 133.07, 122.12, 117.50, 114.42, 112.62 (all Ar-C and pyr-C) ppm. MS (ESI): *m*/*z* = 393.2 [M + H]$^+$, 415.1 [M + Na]$^+$. $C_{24}H_{20}N_6 \cdot 1/2H_2O$ (401.46): calcd. C 71.80, H 5.27, N 20.93; found C 71.64, H 4.77, N 20.89.

Diimine 18: Orange solid, yield 61%. ^1H NMR (400 MHz, [D$_6$]-dmso): δ = 9.15 (d, ^4J = 1.7 Hz, 2 H, Pyr-H), 8.81 (s, 2 H, CH=N), 8.68 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 2 H, Pyr-H), 8.43 (dt, ^3J = 8.0 Hz, ^4J = 1.9 Hz, 2 H, Pyr-H), 7.54 (dd, ^3J = 4.8 Hz, 2 H, ArH), 7.28 (d, ^3J = 8.3 Hz, 2 H, ArH), 7.02 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.84 (d, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 2 H, ArH), 5.45 (s, 4 H, NH_2) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 153.17, 151.25, 150.24, 144.67, 140.12, 134.97, 133.78, 132.25, 123.90, 117.31, 114.38, 112.44 (all Ar-C and pyr-C) ppm. MS (ESI): *m*/*z* = 393.2 [M + H]$^+$, 415.1 [M + Na]$^+$. $C_{24}H_{20}N_6 \cdot 1/3H_2O$ (398.46): calcd. C 72.34, H 5.23, N 21.09; found C 72.41, H 4.69, N 20.88.

Diimine 19: Orange solid, yield 47%. Mixture of two isomers in a 90:10 ratio. ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 8.90 (s, 2 H, CH=N), 8.78 (d, ^3J = 7.8 Hz, ^4J = 2.0 Hz, 2 H, Pyr-H), 8.53 (d, ^3J = 4.6 Hz, ^4J = 2.0 Hz, 2 H, Pyr-H), 7.57 (dd, ^3J = 4.6 Hz, 2 H, ArH), 7.29 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.01 (d, ^4J = 2.0 Hz, 2 H, ArH), 6.83 (d, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 2 H, ArH), 5.55 (s, 4 H, NH$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz; [D$_6$]dmso/[D$_6$]benzene, 90:10): δ = 151.29, 151.13, 150.95, 150.83, 150.71, 150.65, 150.60, 150.55, 149.52, 148.95, 148.53, 148.20, 147.91, 145.28, 145.22, 145.12, 144.29, 143.22, 142.26, 141.05, 140.85, 140.37, 137.65, 137.47, 137.34, 137.25, 135.13, 134.81, 134.68, 133.61, 132.57, 132.06, 130.36, 130.29, 130.19, 130.12, 129.27, 128.87, 128.25, 126.93, 126.50, 123.54, 123.20, 117.34, 117.23, 117.07, 116.96, 115.73, 115.45, 115.30, 114.71, 114.65, 114.28, 114.16, 114.09, 112.77, 112.59, 112.13, 112.00, 111.94 (all Ar-C and pyr-C) ppm. MS (ESI): *m*/*z* = 461.1 [M + H]$^+$, 483.0 [M + Na]$^+$. $C_{24}H_{18}Cl_2N_6 \cdot 1/3H_2O$ (467.35): calcd. C 61.68, H 4.03, N 17.98; found C 61.63, H 3.54, N 17.70.

Standard Protocol for the Syntheses of Tetraimine Ligands: A mixture of 3,3′-diaminobenzidine (typically 0.10–0.20 g, 0.5–0.9 mmol) was dissolved in MeOH (25 mL), and subsequently the appropriate salicylaldehyde (5 equiv.) was added as a solution in $CHCl_3$ (25 mL). The yellow/orange reaction mixture was then stirred for 24 h, and the product collected by concentration, filtration and drying.

Tetraimine 22: Orange solid, yield 64%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.87 (s, 2H OH), 12.81 (s, 2H OH), 8.77 (s, 2 H, CH=N), 8.74 (s, 2 H, CH=N), 7.65 (d, ^4J = 1.9 Hz, ^3J = 8.2 Hz, 2 H, ArH), 7.51 (d, ^4J = 1.9 Hz, 2 H, ArH), 7.48–7.37 (m, 10 H, ArH), 7.05–7.01 (m, 4 H, ArH), 1.36 [s, 18 H, C(CH$_3$)$_3$], 1.34 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 163.7, 162.9, 158.4, 158.3, 142.7, 141.2, 140.9, 140.8, 138.5, 130.3, 130.2, 127.9, 127.8, 124.9, 119.2, 117.7, 117.6, 117.4, 116.3, 115.9, 33.2, 30.6 ppm. MS (ESI): *m*/*z* = 855.4 [M + H]$^+$, 877.4 [M + Na]$^+$. $C_{56}H_{62}N_4O_4$ (855.12): calcd. C 78.66, H 6.55, N 7.31; found C 78.24, H 6.65, N 7.17.

Tetraimine 23: Yellow solid, yield 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.30 (s, 2H OH), 13.27 (s, 2H OH), 8.75 (s, 2 H, CH=N), 8.73 (s, 2 H, CH=N), 7.63 (d, ^4J = 2.0 Hz, ^3J = 8.2 Hz, 2 H, ArH), 7.50 (d, ^4J = 1.9 Hz, 2 H, ArH), 7.38 (d, ^3J = 8.2 Hz, 2 H, ArH), 7.34–7.30 (m, 4 H, ArH), 6.91 (t, ^4J = 1.1 Hz, ^3J = 9.4 Hz, 4 H, ArH), 6.15–6.03 (m, 4 H, C-C=C), 5.17–5.08 (m, 8 H, C-C=C), 3.50 (t, 8 H, C-CH) ppm. The product was too insoluble for ^{13}C NMR measurement. MS (ESI): *m*/*z* = 764.4 [M – C_2H_4]$^+$, 791.3 [M + H]$^+$, 813.3 [M + Na]$^+$. $C_{52}H_{46}N_4O_4 \cdot 1/2H_2O$ (799.95): calcd. C 78.07, H 5.92, N 7.00; found C 78.06, H 5.82 N 7.22.

Tetraimine 24: Yellow solid, yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 13.20 (s, 2H OH), 13.18 (s, 2H OH), 8.74 (s, 2 H, CH=N), 8.72 (s, 2 H, CH=N), 7.63 (d, ^4J = 1.9 Hz, ^3J = 8.2 Hz, 2 H, ArH), 7.48 (d, ^4J = 1.9 Hz, 2 H, ArH), 7.37 (d, ^3J = 8.2 Hz, 2 H, ArH), 6.88 (t, ^4J = 1.2 Hz, ^3J = 7.5 Hz, 4 H, ArH), 2.34 (s, 6 H, CH$_3$), 2.33 (s, 6 H, CH$_3$) ppm. One signal in the ^{1}H NMR spectrum overlaps with the residual solvent signal. The product was too insoluble for ^{13}C NMR measurement. MS (ESI): *m*/*z* = 687.3 [M + H]$^+$, 709.2 [M + Na]$^+$. $C_{44}H_{38}N_4O_4 \cdot H_2O$ (704.80): calcd. C 74.98, H 5.72, N 7.95; found C 75.17, H 5.12, N 8.19.

Syntheses of Bimetallic Complexes

Bis[Zn(salphen)] Complex 25: To a solution of precursor **20** (0.17 g, 0.270 mmol) in $CHCl_3$/MeOH (4:3, 175 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.13 g, 0.59 mmol) in MeOH (10 mL). Directly after the addition of the Zn reagent, an orange suspension was obtained that was stirred for 16 h. Then, the mixture was filtered, and the residue was dried to yield the product as an orange solid (160.3 mg, 0.212 mmol, 78%). ^{1}H NMR (400 MHz, [D$_6$]dmso + 10% [D$_5$]pyridine): δ = 9.29 (br. s, 2 H, CH=N), 9.13 (br. s, 2 H, CH=N), 8.32 (br., 2 H, ArH), 8.03 (br. d, ^3J = 8.2 Hz, 2 H, ArH), 7.86 (br. d, ^3J = 7.9 Hz, 2 H, ArH), 7.53 (br. d, ^3J = 6.9 Hz, 2 H, ArH), 7.48 (br. d, ^3J = 7.4 Hz, 2 H, ArH), 7.27 (br. unresolved t, 4 H, ArH), 6.77 (br. unresolved dd, 4 H, ArH) ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]dmso): δ = 172.4 (CH=N), 163.5, 162.6, 139.8, 138.9, 138.2, 136.4, 136.3, 134.5, 125.7, 123.2, 119.6, 119.5, 116.9, 114.6, 113.1 (all ArC) ppm. MS (MALDI-TOF): *m*/*z* = 758 [M]$^+$. $C_{40}H_{26}N_4O_4Zn_2 \cdot 3.5H_2O$ (757.48): calcd. C 58.55, H 4.05, N 6.83; found C 58.67, H 3.62, N 7.04.

Bis[Zn(salphen)] Complex 26: A solution of 3,5-dinitrosalicylaldehyde (45.2 mg, 0.21 mmol) in MeOH (10 mL) was slowly added to a solution of diimine **2** (50.1 mg, 0.10 mmol) in thf (20 mL). The colour of the solution changed from yellow to red. Then, $Zn(OAc)_2 \cdot H_2O$ (46.7 mg, 0.21 mmol) in MeOH (10 mL) was added, and the colour changed from red to orange. The mixture was stirred for 24 h at room temperature and an orange solid (41.7 mg, 0.040 mmol, 42%) was recovered by filtration. ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 9.48 (s, 2 H, CH=N), 9.02 (s, 2 H, CH=N), 8.86 (d, ^4J = 3.1 Hz, 2 H, ArH), 8.73 (d, ^4J = 3.1 Hz, 2 H, ArH), 8.38 (s, 2 H, ArH), 8.06 (d, ^3J = 8.7 Hz, 2 H, ArH), 8.01 (d, ^3J = 9.4 Hz, 2 H, ArH), 7.33 (d, ^3J = 7.7 Hz, 2 H, ArH), 7.28 (d, ^3J = 7.3 Hz, 2 H, ArH), 6.50 (t, ^3J = 7.5 Hz, 2 H, ArH), 1.46 [s, 18 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]dmso): δ = 172.20, 166.95, 163.89, 162.12, 142.49, 141.67, 140.00, 138.68, 137.75, 135.75, 134.79, 131.69, 131.04, 127.56, 123.98, 122.51, 119.46, 117.47, 115.41, 112.79, 67.02, 34.92, 29.56, 25.13 ppm. MS (MALDI-TOF): *m*/*z* = 1049 [M + H]$^+$, 1033 [M – CH$_3$]$^+$. $C_{48}H_{38}N_8O_{12}Zn_2 \cdot$thf (1121.79): calcd. C 55.68, H 4.13, N 9.99; found C 55.10, H 4.25, N 9.91.

Bis[Zn(salphen)] Complex 29: To a solution of 3,3′-diaminobenzidine (98.6 mg, 0.46 mmol) and 3-nitrosalicylaldehyde (372.7 mg, 2.23 mmol) in $CHCl_3$/MeOH (7:3, 100 mL) was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.50 g, 2.3 mmol) in MeOH (10 mL). The suspension obtained was stirred for 16 h and then filtered. The residue was successfully washed with MeOH and acetone and then dried to yield the crude product as a dark orange/brown solid (393.9 mg, 0.42 mmol, 91%). Extraction with thf afforded the title compound as an analytically pure, bright orange solid. ^{1}H NMR (400 MHz, [D$_6$]dmso): δ = 9.26 (s, 2 H, CH=N), 9.14 (s, 2 H, CH=N), 8.32 (d, ^4J = 1.1 Hz, 2 H, ArH), 8.04 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.95 (d, ^3J = 8.4 Hz, ^4J = 1.5 Hz, 2 H, ArH), 7.88–7.85 (dt, ^3J = 7.8 Hz, ^4J = 2.2 Hz, 4 H, ArH), 7.82–7.77 (dt, ^3J = 7.7 Hz, ^4J = 2.0 Hz, 4 H, ArH), 6.60 (pseudo q, ^3J = 6.6 Hz, ^4J = 2.2 Hz, 4 H, ArH) ppm. The product was too insoluble for proper ^{13}C NMR measurement. MS (MALDI-TOF): *m*/*z* = 959 [M + Na]$^+$. $C_{40}H_{22}N_8O_{12}Zn_2 \cdot 3thf\cdot H_2O$ (1171.80): calcd. C 53.30, H 4.13, N 9.56; found C 53.25, H 4.38, N 9.53.

Bis[Zn(salphen)] Complex 30: A solution of 3,5-dinitrosalicylaldehyde (65.9 mg, 0.31 mmol) in MeOH (10 mL) was slowly added to a solution of diimine **1** (50.7 mg, 0.078 mmol) in $CHCl_3$ (25 mL). The colour of the solution changed from yellow to red-orange. Then, $Zn(OAc)_2 \cdot H_2O$ (68.1 mg, 0.31 mmol) in MeOH (10 mL) was added, and the mixture was stirred for 24 h at room temperature. An orange solid (77.2 mg, 0.067 mmol, 85%) was recovered by filtration. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 (s, 2 H, CH=N), 9.06 (s, 2 H, CH=N), 8.87 (d, ^4J = 3.1 Hz, 2 H, ArH), 8.73 (d, ^4J = 3.0 Hz, 2 H, ArH), 8.38 (s, 2 H, ArH), 8.09 (d, ^3J = 8.8 Hz, 2 H, ArH), 8.01 (d, ^3J = 8.5 Hz, 2 H, ArH), 7.37 (d, ^4J = 2.5 Hz, 2

H, ArH), 7.29 (d, ^4J = 2.4 Hz, 2 H, ArH), 1.48 [s, 18 H, $C(CH_3)_3$], 1.30 [s, 18 H, $C(CH_3)_3$] ppm. The product was too insoluble for proper ^{13}C NMR analysis. MS (MALDI-TOF): *m*/*z* = 1160 $[M]^+$. $C_{56}H_{54}N_8O_{12}Zn_2 \cdot 2H_2O$ (1197.89): calcd. C 56.15, H 4.88, N 9.35; found C 56.02, H 4.93, N 9.24.

Bis[Zn(salphen)] Complex 31: A solution of 3,5-dichlorosalicylaldehyde (32.8 mg, 0.17 mmol) in MeOH (10 mL) was slowly added to a solution of diimine **1** (50.0 mg, 0.077 mmol) in $CHCl_3$ (25 mL). The colour of the solution changed from yellow to red-orange. Then, $Zn(OAc)_2 \cdot H_2O$ (38.4 mg, 0.17 mmol) in MeOH (10 mL) was added, and the mixture was stirred for 24 h at room temperature. An orange solid was recovered by filtration. Yield: 63.9 mg (0.057 mmol, 75%). ^1H NMR (400 MHz, [D$_6$]dmso): δ = 9.25 (s, 2 H, CH=N), 9.04 (s, 2 H, CH=N), 8.28 (s, 2 H, ArH), 8.05 (d, ^3J = 8.8 Hz, 2 H, ArH), 7.92 (d, ^3J = 8.4 Hz, 2 H, ArH), 7.60 (d, ^4J = 2.8 Hz, 4 H, ArH), 7.55 (d, ^4J = 2.8 Hz, 2 H, ArH), 7.35 (d, ^4J = 2.5 Hz, 2 H, ArH), 7.27 (d, ^4J = 2.4 Hz, 2 H, ArH), 1.50 [s, 18 H, $C(CH_3)_3$], 1.30 [s, 18 H, $C(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 170.61, 164.46, 163.80, 162.12, 140.91, 139.87, 139.05, 137.60, 133.64, 133.21, 132.24, 129.62, 128.87, 127.05, 126.53, 120.57, 118.24, 117.21, 114.84, 114.56, 35.12, 33.59, 31.33, 29.61 ppm. MS (MALDI-TOF): *m*/*z* = 1118 $[M]^+$. $C_{56}H_{54}Cl_4N_4O_4Zn_2$ (1119.68): calcd. C 60.07, H 4.86, N 5.00; found C 59.84, H 5.01, N 4.84.

Bis[Zn(salphen)] Complex 34: A solution of 5-trimethylsilylacetylsalicylaldehyde (46.8 mg, 0.21 mmol) in MeOH (10 mL) was slowly added to a solution of diimine **2** (51.7 mg, 0.10 mmol) in thf (50 mL). The colour of the solution changed from yellow to orange. Then, $Zn(OAc)_2 \cdot H_2O$ (47.8 mg, 0.22 mmol) in MeOH (10 mL) was added, and the colour changed from orange to red. The mixture was stirred for 24 h at room temperature and an orange solid (55.1 mg, 55%) was recovered by filtration. ^1H NMR (400 MHz, [D$_6$]dmso): δ = 9.23 (s, 2 H, CH=N), 9.03 (s, 2 H, CH=N), 8.23 (s, 2 H, ArH), 8.01 (d, ^3J = 8.7 Hz, 2 H, ArH), 7.90 (d, ^3J = 7.5 Hz, 2 H, ArH), 7.75 (d, ^4J = 2.2 Hz, 2 H, ArH), 7.29 (m, 6 H, ArH), 6.64 (d, ^3J = 8.8 Hz, 2 H, ArH), 6.47 (t, ^3J = 7.5 Hz, 2 H, ArH), 1.48 [s, 18 H, $C(CH_3)_3$], 0.21 [s, 18 H, $Si(CH_3)_3$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, [D$_6$]dmso): δ = 172.46, 172.19, 163.30, 162.60, 141.42, 141.00, 139.49, 139.41, 137.88, 136.52, 134.60, 130.60, 126.07, 123.97, 119.67, 119.47, 117.06, 114.54, 112.41, 106.50, 105.92, 90.40, 30.67, 22.16, 0.24 ppm. MS (MALDI-TOF): *m*/*z* = 1062 $[M]^+$, 1047 $[M - CH_3]^+$. $C_{58}H_{58}N_4O_4Si_2Zn_2 \cdot 3H_2O$ (1116.10): calcd. C 62.41, H 5.78, N 5.02; found C 62.06, H 5.51, N 4.90.

Crystallographic Studies: Measured crystals were prepared under inert conditions immersed in perfluoropolyether as protecting oil for manipulation. Measurements were made with a Bruker-Nonius diffractometer equipped with an APPEX 2 4 K CCD area detector, a FR591 rotating anode with Mo-K_α radiation, Montel mirrors as monochromator and a Kryoflex low-temperature device (T = –173 °C). Full-sphere data collection was used with ω and ϕ scans. Data collection was performed with Apex2 V. 1.0–22 (Bruker-Nonius 2004), data reduction was performed with Saint + Version 6.22 (Bruker-Nonius 2001) and absorption correction was performed with SADABS V. 2.10 (2003). SHELXTL Version 6.10 (Sheldrick, 2000) was used for structure solution and refinement.

Comments for 26: As a result of technical complications, only half the data set could be measured for this crystal (61% of completeness). Further attempts to obtain a full data set of this structure were not successful, as recrystallization provided crystals of lower quality that were not useful for structure determination. Despite the lack of data, the structure is of high-enough quality to be reported. The refined structure contains two half independent molecules (both with C_i symmetry) in the unit cell of the main complex and six positions of dmso molecules with a total occupancy of five and half solvent molecules for each two half molecules of complex. In three of the located positions, the dmso molecules are disordered in different orientations and occupation ratios. One of the disordered dmso molecules takes three different orientations with an occupation ratio of 59:26:25. In spite of the correlation effects and further difficulties in the refinement of the structure, the program SQUEEZE[23] was not used to omit solvent molecules, as some of them have direct interactions with the Zn atoms of the main complex.

Comments for 30: The unit cell contains nine positions for dmso molecules with a total occupancy of eight and half molecules for each molecule of complex. In five of the located positions the dmso molecules are disordered in different orientations and occupation ratios. Additionally, also a molecule of water could be detected. Although the high number of disordered molecules complicated the refinement of the structure, the use of the SQUEEZE[23] program to omit the solvent molecules was avoided in this case, as some of the solvent molecules have direct interactions with the Zn atoms of the metal complex.

Comments for 31·bipy: The unit cell contains the building block of a linear polymer. For each fragment of polymer, five molecules of thf were detected. The solvent molecules are partially disordered showing the typical effects of pseudorotation observed in nonrigid cyclic rings. One of the thf molecules is disordered in three positions. The omission of the solvent molecules with the SQUEEZE[23] program did not significantly improve the statistics and the disorder model was preferred for the structure refinement, in spite the fact that some of the atoms had large thermal displacement parameters.

CCDC-679911, -679912 and -679913 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.

Supporting Information (see footnote on the first page of this article): ^1H NMR spectra of compounds **1**, **2**, **3**, **9**, **23**, **24**, **29**, **31**, **32**; comparison integral ratios between the imine and OH regions of compounds **1**, **5**, **8**.

Acknowledgments

The authors wish to thank Institució Catalana de Recerca i Estudis Avançats (ICREA) and Institute of Chemical Research of Catalonia (ICIQ) for generous support of this work. A. W. K. is an ICREA fellow. Dr. Jonathan Barr, Joan Salles, Lora Farjon and Dr. Noemí Cabello are thanked for the mass spectrometric studies. Kerman Gómez and Dr. Gabriel Gonzàlez are acknowledged for their help with the ^1H DOSY NMR experiments.

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[16] Crystal data for compound **26**: Formula $2(C_{52}H_{50}N_8O_{14}S_2Zn_2)\cdot 7(C_2H_6OS)$, M = 2958.81, monoclinic, $C2/c$ (No. 15), a = 36.4392(10) Å, b = 9.5882(3) Å, c = 38.4521(11) Å, β = 99.921(1)°, V = 13233.7(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.485 g/cm^3, $F(000)$ = 6152, crystal size 0.15 × 0.20 × 0.30 mm, T = 100 K, θmin–max = 2.7–35.8°, total/unique data = 34311/18891, R_{int}= 0.046, observed data [$I > 2.0\sigma(I)$] = 12770, N_{ref}/N_{par} = 18891/894, $R/wR/S$ = 0.0588/0.1607/1.03, max. and av. shift/error = 0.00, 0.00, min. and max. resd. dens. = –0.74, 1.88 e/Å^3.

[17] Crystal data for compound **30**: Formula $(C_{60}H_{66}N_8O_{14}S_2Zn_2)\cdot 12(C_2H_6OS)\cdot(C_2H_6OS)\cdot 2(H_2O)$, M = 3688.09, triclinic, $P\bar{1}$ (No. 2), a = 14.7497(9) Å, b = 16.5770(9) Å, c = 19.9117(12) Å, α = 79.456(3)°, β = 74.018(3)o, γ = 73.347(3)°, V = 4455.3(5) Å^3, Z = 1, $\rho_{calcd.}$ = 1.375 g/cm^3, $F(000)$ = 1938, crystal size 0.10 × 0.20 × 0.30 mm, T = 100 K, θmin–max = 2.6–31.3°, total/unique data = 65510/26748, R_{int} = 0.052, observed data [$I > 2.0\sigma(I)$] = 17287, N_{ref}/N_{par} = 26748/1069, $R/wR/S$ = 0.0855/0.2670/1.03, max. and av. shift/error = 0.00, 0.00, min. and max. resd. dens. = –3.31, 2.50 e/Å^3.

[18] Crystal data for compound **31**·bipy: Formula $(C_{33}H_{31}Cl_2N_3O_2Zn)\cdot 5(C_4H_8O)$, M = 998.42, triclinic, $P\bar{1}$ (No. 2), a = 9.6480(6) Å, b = 16.1632(9) Å, c = 17.5764(9) Å, α = 87.570(3)°, β = 74.285(3)°, γ = 74.177(3)°, V = 2537.0(3) Å^3, Z = 2, $\rho_{calcd.}$ = 1.307 g/cm^3, $F(000)$ = 1060, crystal size 0.05 × 0.05 × 0.40 mm, T = 100 K, θmin–max = 2.8–30.9°, total/unique data = 23805/13472, R_{int}= 0.048, observed data [$I > 2.0\sigma(I)$] = 9787, N_{ref}/N_{par} = 13472/696, $R/wR/S$ = 0.0696/0.2116/1.04, max. and av. shift/error = 0.00, 0.00, min. and max. resd. dens. = –1.21, 2.00 e/Å^3.

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Received: March 14, 2008
Published Online: May 20, 2008

