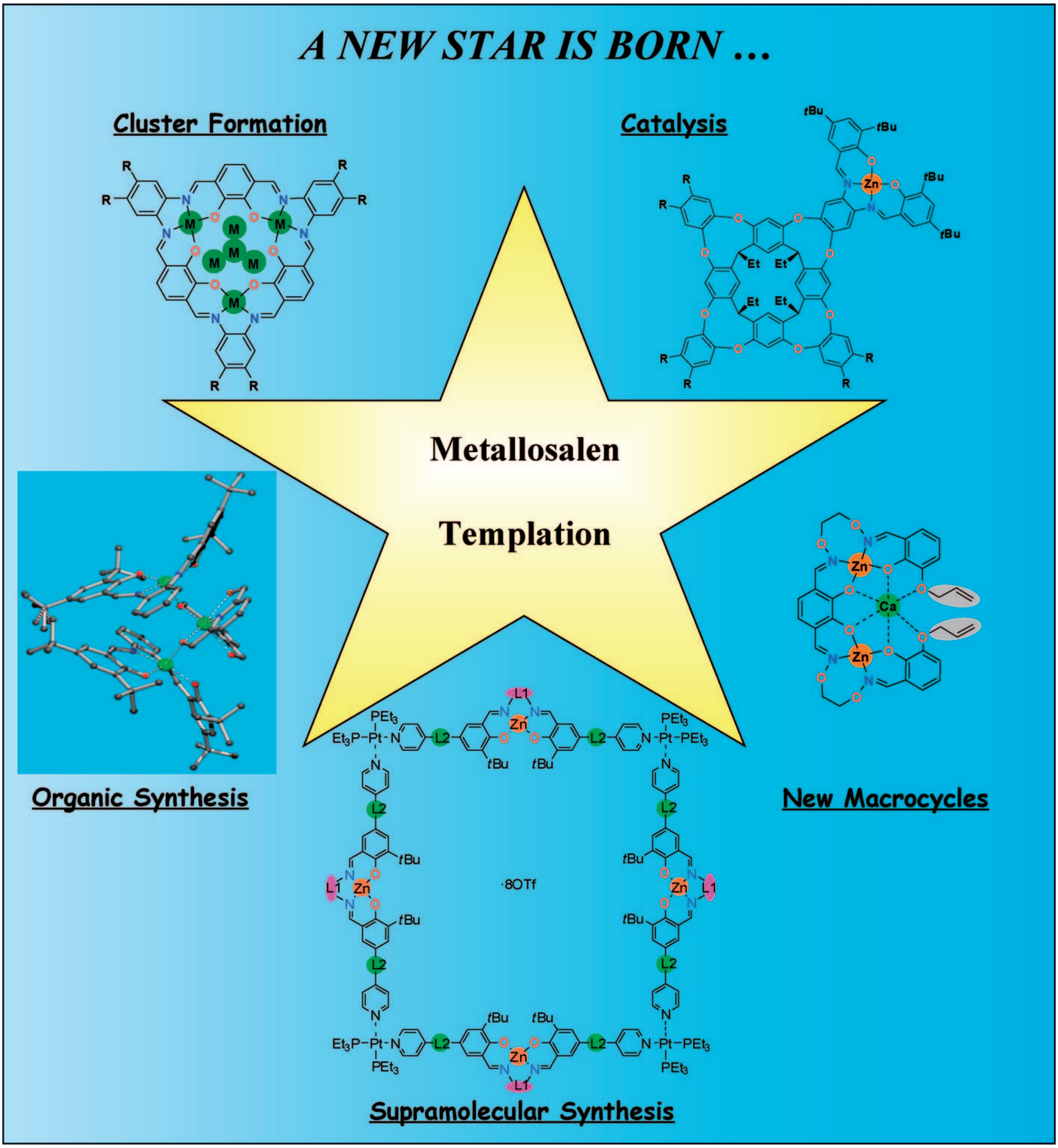
CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200801149

New Templating Strategies with Salen Scaffolds (Salen = *N*,*N*′-Bis(salicylidene)ethylenediamine Dianion)

Arjan W. Kleij*[a, b]



Abstract: Templated approaches towards selective organic synthesis is a common feature in nature in which nucleic acid templated synthesis plays a crucial role in various fundamental biological processes. The key feature that allows control over the amazing selectivity found in natural processes is evidently the effective molarity of the reaction partners that is mediated by the macromolecular templation event. An ongoing challenge within many chemical sciences is to exploit similar templating principles and make use of synthetic systems that are designed for specific chemical conversions. Here, we describe the recent developments that involve (metallo)salen scaffolds that are used for diverse templating events (salen = *N*,*N'*-bis(salicylidene)ethylenediamine dianion).

Keywords: macrocycles • organic synthesis • salen • supramolecular chemistry • templates

Introduction

Proper modulation of the process parameters of chemical reactions provides a means towards selective synthesis. Within the fields of organic synthesis and homogeneous catalysis precise control over the reactivity of the involved species leads to the desired target molecules, usually at mM to M concentration regimes. However, when multiple reaction partners are present in the same phase, substrate selectivity becomes a crucial factor to control. Nature, in contrast to synthesis carried out by chemists, takes advantage of a different approach towards selective synthesis under much more dilute conditions (nM to μM). The control over the reactivity of particular molecules is directed through macromolecular templation. The involved macromolecule brings together certain combinations of reactive molecules which enables biomolecular synthesis of the required products as a result of the increase in the effective molarity (EM) and hence efficient and selective conversions are achieved.[1]

Salen scaffolds are popular ligand structures that are of great value to the homogeneous catalysis community.[2] Ever since the pioneering work of Jacobsen and Katsuki in the enantioselective epoxidation of unfunctionalised olefins,[3] metallosalen complexes (salen = *N*,*N'*-bis(salicylidene)ethylenediamine dianion) have been utilised as efficient catalysts in various organic conversions. However, the use of salen scaffolds in applications that go beyond their conventional use in homogeneous catalysis has recently aroused much interest.[4] In particular, new multimetallic, macrocyclic and supramolecular systems have emerged in which salen fragments largely dictate the material properties. The ease with which the salen structure can be derivatised makes it an ideal building block for sophisticated assembled constructs. Clear advantages over similar planar, tetradentate dianionic ligands such as porphyrins are: a) the access to relative large amounts of a diverse library of synthetic intermediates that can be obtained in few steps, b) the straightforward introduction of chiral modules within the salen unit, and c) the flexibility of changing either one or both phenyl side groups (both sterically as well as electronically)[5] and the bridging unit. This creates a large potential for fine-tuning the interactions of the (metallo)salen unit with other molecules, and the construction of new materials with interesting catalytic[6] and/or photophysical features.[7] Typical examples of new composites that comprise one or multiple salen frameworks include DNA-salen hybrids,[8] alkaloid adsorption materials[9] and interesting allosteric catalyst systems.[10] Here, we explicitly focus on the use of (metallo)salen-containing structures in which the salen unit is actively involved in directed, templated synthesis. Intriguing illustrations of the effective use of salen groups as molecular templates in synthetic strategies will be presented, and the role of the metal ion in the templating events is also highlighted.

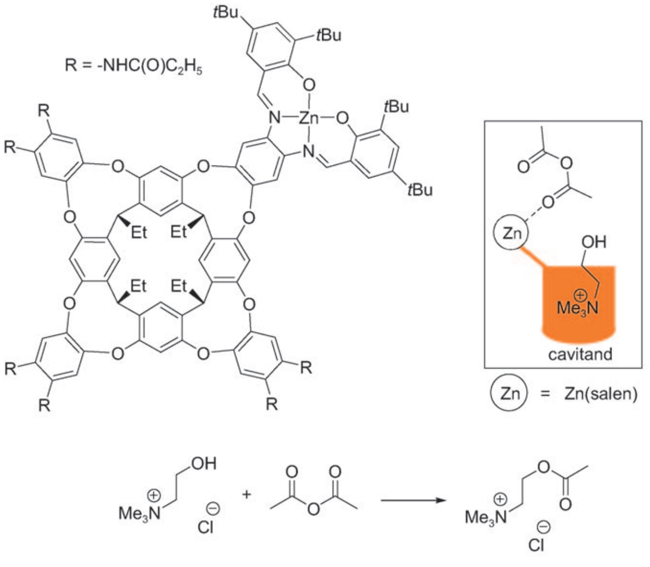
Salen-Templated Catalysis

One of the earliest examples of a salen template effect in homogeneous catalysis was reported by Rebek and co-workers.[11] They designed and utilised a Zn^{II}salen-modified cavitand structure (Scheme 1) for the directed synthesis of acetylcholine from choline and acetic anhydride. The Zn(salen) unit was positioned on the periphery of the cavitand structure in such a way that it could template the catalytic process making use of the binding pocket. The proposed catalytic process starts off with the encapsulation of the choline substrate by the cavitand structure and the simultaneous activation of the acetic anhydride by the Zn(salen) fragment. In the absence of the Zn(salen) complex, the acylation of choline is very slow, but the reaction is significantly promoted by the presence of the Zn(salen) unit (2 mol%) with a rate enhancement of 1900-fold compared to the background reaction. Additionally, it was demonstrated that a combination of non-modified cavitand and "free" Zn(salen) complex gives a lower acylation rate, which demonstrates the complementing nature of both modules. If sterically more demanding substrates (i.e., anhydrides) were used, slower kinetics were observed, which can be reasoned by assuming a weaker interaction with the Zn^{II} metal centre.

---

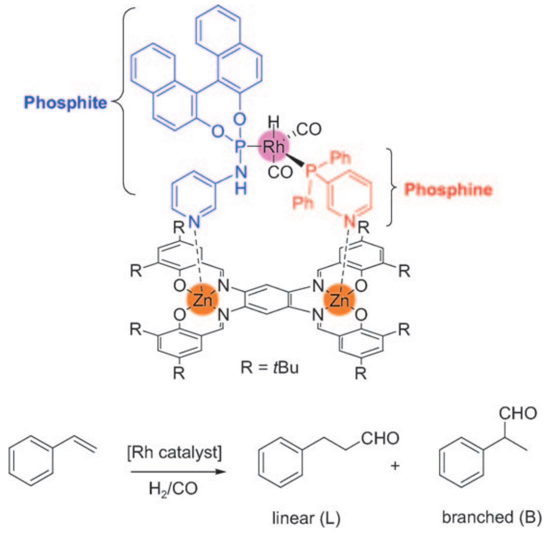
[a] Dr. A. W. Kleij
Institute of Chemical Research of Catalonia (ICIQ)
Av. Països Catalans 16, 43007 Tarragona (Spain)
Fax: (+34) 977-920-224
Homepage: www.iciq.es
E-mail: akleij@iciq.es

[b] Dr. A. W. Kleij
Institució Catalana de Recerca i Estudis Avançats (ICREA)
Lluis Companys 23, 08010 Barcelona (Spain)



Scheme 1. Salen-cavitand structure employed by Rebek for the accelerated formation of acetylcholine.

In another contribution, Reek et al. have shown that hetero-bidentate ligands based on the combination of various phosphites and phosphines may be accessed by using a bimetallic Zn(salphen) template (salphen = *N*,*N*′-1,2-phenylenebis(salicylideneimine)).[12] The Zn^{II} centres within the N_2O_2 cavities of the salen units here serve as a Lewis acid sites that can be axially coordinated by pyridine donors. Thus, phosphites and phosphines equipped with such donor fragments were prepared and equimolar mixtures (2 equiv of the mixed ligand species) were combined with the bis-Zn(salphen) template. Surprisingly, in all reported cases the exclusive formation of the heterocombination was observed (Scheme 2). In the absence of the bis-Zn(salphen) template, or by simply using mono-Zn(salphen)/phosphine or mono-Zn(salphen)/phosphite combinations only formation of the homocomplexes was noted. The main argument put forward by the authors for the formation of heterobidentate templated structures is that there exists a delicate relationship between the reorganisation energy (going from non-templated to templated) and the steric impediment of the involved ligands. A series of phosphite/phosphine ligands were then combined with the bis-Zn(salphen) template and a suitable Rh^I precursor to allow the formation of a range of different (pre)catalysts that were screened in the asymmetric hydroformylation of styrene (Scheme 2). Without the bis-Zn(salphen) template, both phosphite as well a phosphine ligands proved to be inferior to the templated heterobidentate system, and particularly in terms of enantioselectivity. A very low chiral induction was observed in these non-templated homocombinations, whereas for a number of templated heterobidentate systems asymmetric induction of up to 72 % could be achieved.



Scheme 2. Typical example of a template-induced formation of heterobidentate ligands and its Rh^I complex using a bis-Zn(salphen) complex.

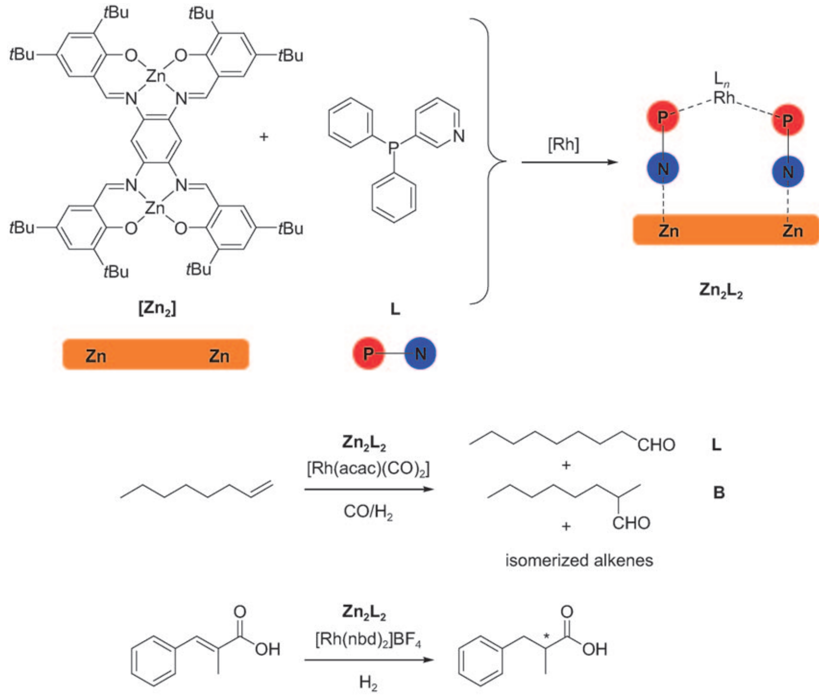
Following a similar strategy, Reek and co-workers also communicated the template-assisted formation of bidentate systems based on homo-couples of pyridine-derived phosphine or phosphite ligands.[13] A rigid bis-Zn(salphen) complex was used as a molecular template (Scheme 3), onto which two equivalents of the respective pyridine phosphorus ligands were immobilised following complexation with a suitable transition metal precursor. The resultant supramolecular complexes were tested in the (asymmetric) hydroformylation and hydrogenation and compared to the non-templated catalysts and catalysts derived from the 2:2:1 combination mono-Zn(salphen)/phosphorus ligand/metal precursor. The catalytic results with the templated catalysts affirmed that in nearly all cases a typical bidentate behaviour was operative. Only marginally better results were obtained in terms of conversion rate and linear to branched ratios (L/B ratio) for the hydroformylation of 1-octene (Scheme 3), whereas the asymmetric hydroformylation of styrene (see Scheme 2) provided a few examples with a slight increase in enantiomeric excess (*ee*) upon templation. The same holds for the asymmetric hydrogenation of α-methylcinnamic acid using these supramolecular catalysts; some minor improvement of the enantioselectivity (maximum $\Delta ee \approx 10\,\%$) was noted for the templated catalysts though at a very low conversion stage. The similar results for the non-templated and templated catalysts seem to indicate that for the derived Rh^I complexes comparable intermediates (i.e., geometries) are involved in the different catalytic reactions. A major advantage of this approach is that the available amount of building blocks may be extended with relative ease allowing for the formation of a larger set of self-assembled catalysts. In this way, optimisation of organic conversions can be foreseen by using high-throughput experimentation methods.

Formation of Functional Macrocycles

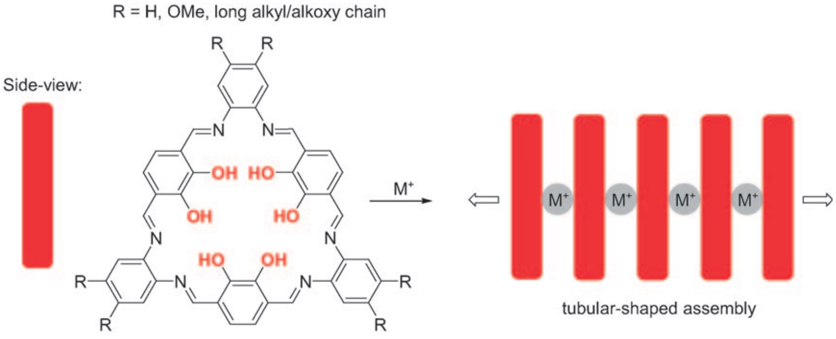
The (self)assembly of rigid, shape-persistent macrocycles into functional materials remains a challenging goal within the field of supramolecular chemistry. Promising applications that may arise by using such macrocyclic systems involve synthetic mimics for ion-conducting channels, tubular structures and porous materials. Recently, macrocyclic salen frameworks[14] have been recognised as interesting structures that resemble crown ethers to a certain extent, owing to the presence of multiple O-donor atoms arranged in a cyclical fashion. In particular, the groups of MacLachlan and Nabeshima have been involved in the construction and detailed studies of triangular shaped trisalphen macrocycles (Scheme 4).

The group of MacLaclan reported the alkali metal induced or salen macrocycle templated formation of tubular networks (Scheme 4).[15] Various cations (Li^+, Na^+, K^+, Cs^+, Rb^+ and NH_4^+) were tested, and titration experiments (NMR and UV/Vis spectroscopy) confirmed the formation of an assembled superstructure. Detailed NMR and ES-MS studies supported the assembly formation by interaction of the cations with the phenolic O-atoms of the salen units, thereby thus behaving as crown ether derivatives. In the assembled species, the different trisalphen units are stacked with each other and the size of the cation proved to be a decisive connecting element as observed by the relative NMR shielding features upon formation of the tubular architecture.

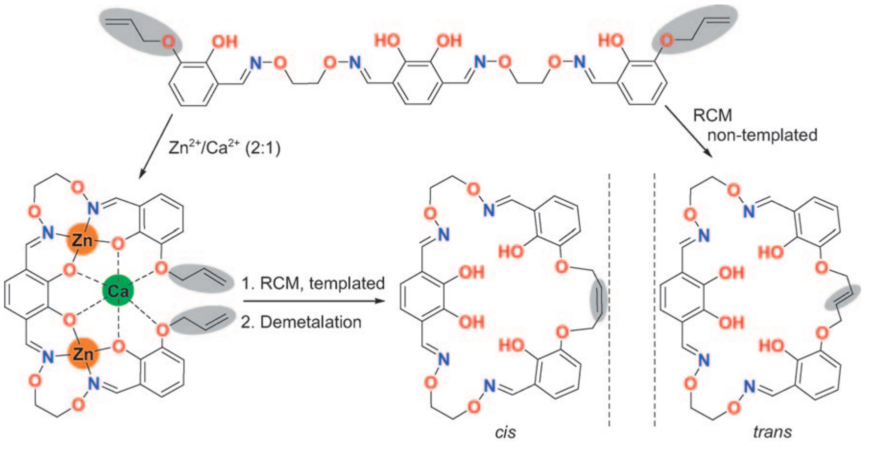
A templated approach toward the synthesis of oxime-based salen type macrocycles was reported by Nabeshima et al.[16] Here, a 32-membered macrocycle could be produced by ring-closing methathesis (RCM) of pendant allyloxy groups at both ends of a linear oxime-derived ligand system (Scheme 5).



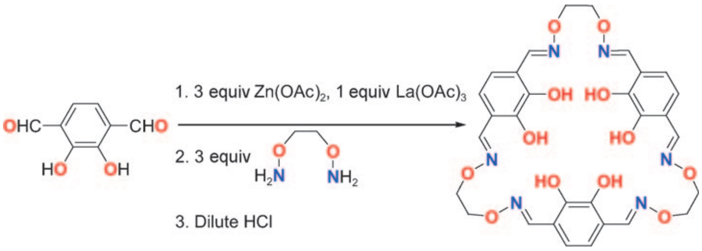
Scheme 3. Representative example of a template-induced formation of homobidentate ligands and its Rh^I complex using a bis-Zn(salphen) complex. Catalytic behaviour was tested in the (asymmetric) hydroformylation and hydrogenation.



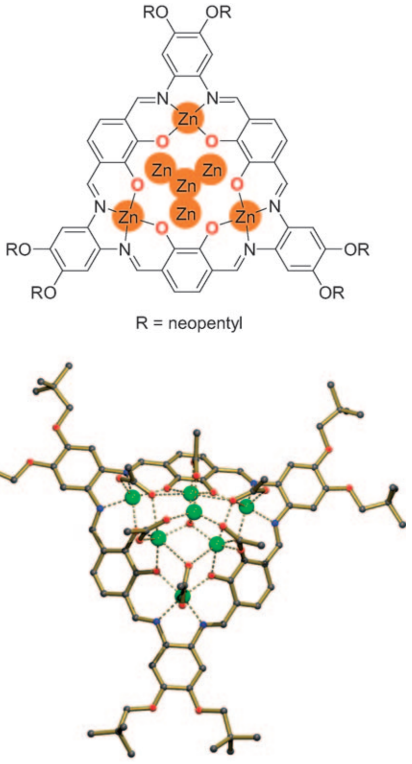
Scheme 4. Schematic representation of the salen-mediated formation of stacked, tubular networks in the presence of cations.



Scheme 5. Templated approach towards the formation of a macrocyclic oxime-based salen-type structure; the templated approach almost exclusively yields the *cis* isomer.



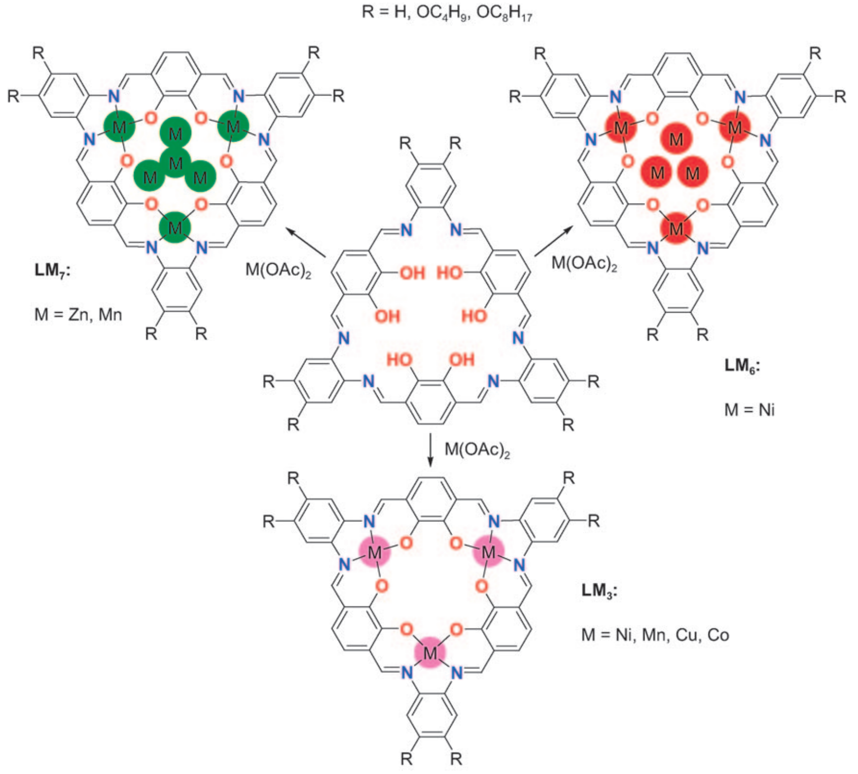
Scheme 6. Synthesis of a hexaoxime, macrocyclic salen-type structure using a templated approach.



Scheme 7. Schematic view of the cluster compound (at the top) starting from a macrocyclic trisalphen framework. Below, the X-ray molecular structure of the bowl-shaped, polynuclear $[Zn]_7$ compound. Colour codes: Zn = green, O = red, N = blue.

The metalation of the linear oxime-salen ligand (L) with a 2:1 mixture of Zn^{II} and Ca^{II} ions selectively affords the mixed heterotrimetallic synthon (LZn_2Ca).[17] The latter structure preorganises the pendant allyloxy groups in a way that upon the RCM reaction only the *cis* isomer (Scheme 5) is obtained as opposed to the (expected) *trans* isomer produced by means of the non-templated reaction.

In a separate contribution,[18] the same authors also reported the [Zn+La]-mediated templated formation of a 36-membered macrocyclic hexaoxime salen-type structure (Scheme 6) using a one-pot procedure. The product was obtained quantitatively by this formal [3+3] condensation reaction in the presence of the Zn and La cations, whereas the yield was very low in the absence of these cations. The oxime-based macrocycle is an interesting platform for the formation of homometallic (Zn_6) or heterometallic (Zn_3La) cluster compounds (vide infra) through either in situ formation or isolation of the non-metalated macrocycle (Scheme 6) and re-metalation under appropriate conditions.

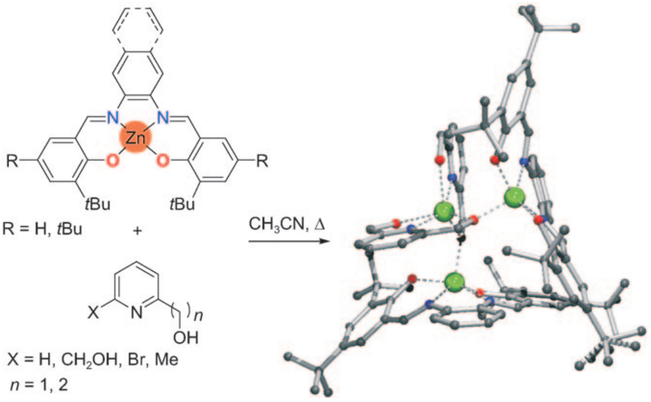


Scheme 8. Multinuclear metallomacrocycles based on a trisalphen structure using various metal acetate salts.

Templated (In)Organic Synthesis

Templated organic synthesis, as briefly discussed in the introduction, is a common feature encountered in nature to control chemical reactivity. Contemporary chemists intend to use similar approaches in multiple disciplines to arrive at new materials that show unusual properties. In this section, a focus is made on templated inorganic/organic synthesis using a metallosalen-mediated approach.

An interesting salen template effect was noted by the groups of MacLachlan and Nabeshima[14d,19] who simultaneously reported that the use of triangular



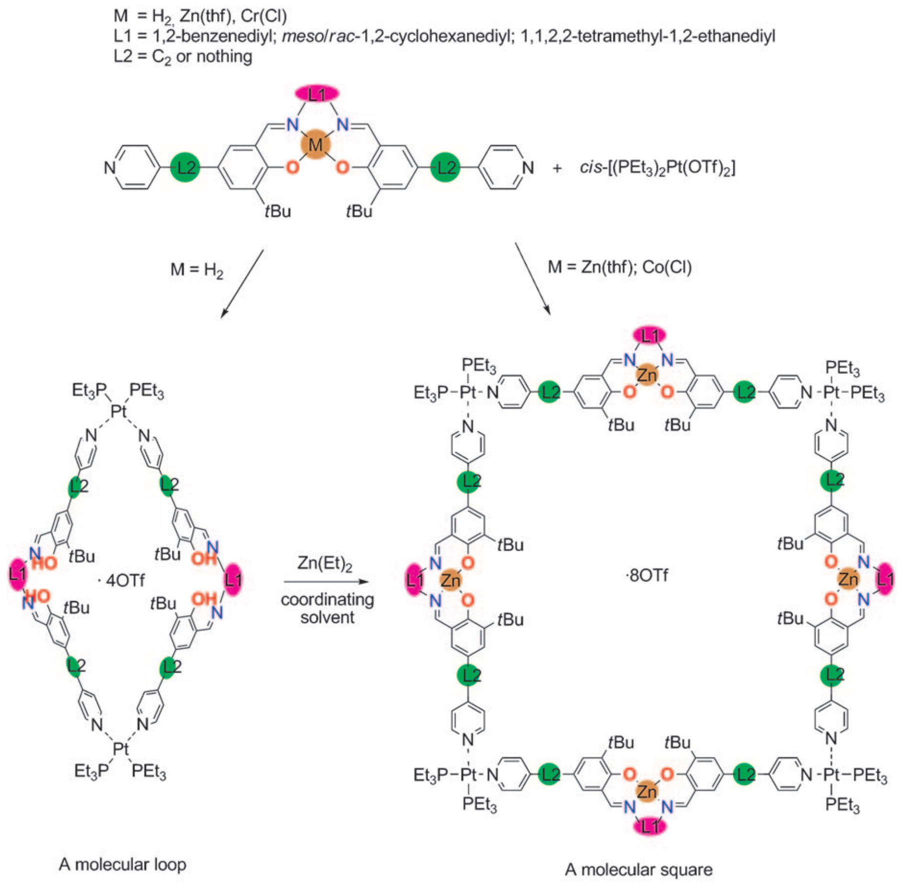
Scheme 9. Formation of an unusual tri-Zn supramolecular assembly by selective mono-deprotonation of a bis-2,6-methanol-pyridine ligand. Zn = green, O = red, N = blue.

shaped salen macrocycles (Scheme 4) were useful as templating platforms for the build up of metal cluster compounds. For instance, Zn-centred macrocycles are valuable model species for the active sites of metalloenzymes such as alkaline phosphatise, P1 nuclease and phospholipase C;[20] the latter two enzymes are known to have trinuclear Zn-clusters in the active site. Other uses may be found in the development of materials with interesting magnetic and/or photophysical properties. In this sense it is important to note that the successful incorporation of different metal ions in these trisalphen macrocycles offers a great potential.

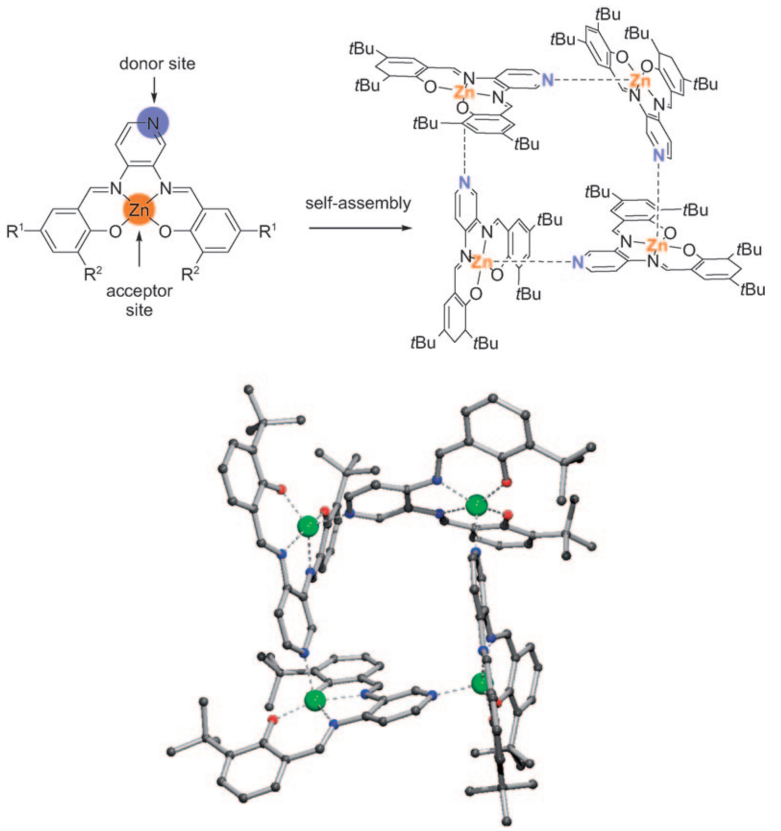
Zinc carboxylate cluster formation was noted when a trisalphen macrocycle (Scheme 4) was treated with a slight excess of zinc acetate.[19] The cluster derivative can be split in two separate modules; the trisalphen-Zn$_3$ core unit which in fact acts as the templating system, and a second part that has a tetrahedral $[Zn_4(\mu_4\text{-}O)]^{6+}$ unit very similar to basic zinc acetate.[21] In these type of aggregates, the acetate ligands are bridging the Zn^{2+} centres in a μ-1,2 fashion (X-ray structure, Scheme 7). Mechanistic studies have revealed that the formation of the cluster derivative probably takes place via a tetrazinc intermediate, which could also be trapped and fully characterised. Upon treatment of the tetrazinc intermediate with three equivalents of zinc acetate, the heptanuclear complexes was produced. The tetrazinc intermediate species also provided a useful platform for the introduction of other metal ions (i.e., mixed metal cluster formation), and preliminary experiments have indicated that cobalt clusters of type $[Co_4O]^{6+}$ can also be incorporated in the trisalphen-Zn$_3$ macrocycle.

Nabeshima and co-workers[14d] have used a similar approach towards cluster formation based on similar trisalphen macrocycles, and examined the influence of the type of metal ion on the cluster formation (Scheme 8). Whereas in the presence of 7 equiv of zinc acetate the heptanuclear complex (Scheme 7) was formed in high yield, only trinuclear complexes were formed using either cobalt(II) acetate or copper(II) acetate, even in the presence of an excess of the metal reagent. For the analogous manganese(II) and nickel(II) salts, various multinuclear compounds could be isolated depending on the reaction stoichiometry. The trinuclear Mn^{II} complex proved to be rather oxidation sensitive and rapidly interconverts into its (poly)Mn^{III} derivative. The tri-Co^{II} trisalphen macrocycle is more stable towards auto-oxidation but may be readily oxidised by air to afford the corresponding Co^{III} complex.

A zinc(II)salphen-templated synthesis of non-symmetrical pyridine ligands was reported by Kleij et al.[22] The high Lewis acidity of the Zn^{2+} ion in these salphen complexes offers a



Scheme 10. Formation of loop and square type supramolecular assemblies using a salen-directed approach. The coordination sphere around the Zn ions is completed by THF.



Scheme 11. Top: A self-assembled tetrameric Zn(salen) complex equipped with a donor and an acceptor site. Bottom: the determined X-ray molecular structure. Zn = green, O = red, N = blue.

large potential for their use in catalytic processes by activation of coordinated functional groups. Pyridine ligands that are *ortho*-substituted with methanolic fragments are conveniently mono-deprotonated by the Zn(salphen) complex eventually leading to the formation of unusual tri-Zn supramolecular assemblies (Scheme 9).

The assembly based on a 2,6-dimethanolpyridine ligand (Scheme 9; R = *t*Bu, X = CH_2OH, X-ray structure) is build up from a central, non-symmetrical unit consisting of a distorted octahedral Zn^{2+} ion ligated by two mono-deprotonated pyridine-dimethanol ligands. The anionic O-donor atoms of both pyridine systems further coordinate to a Zn(salphen) complex. Interestingly, when dimeric Zn(salphen) derivatives were employed,[23] the formation of a similar tri-Zn assembly was completely prevented. The projected formation mechanism of these trinuclear complexes starts off with the initial coordination of the OH fragment to the metal centre, which is unable to compete with the monomer$\rightleftharpoons$dimer equilibrium for dimeric Zn(salen) derivatives. Further experiments have revealed a wider scope of the activation of various methanol-substituted pyridine ligands.

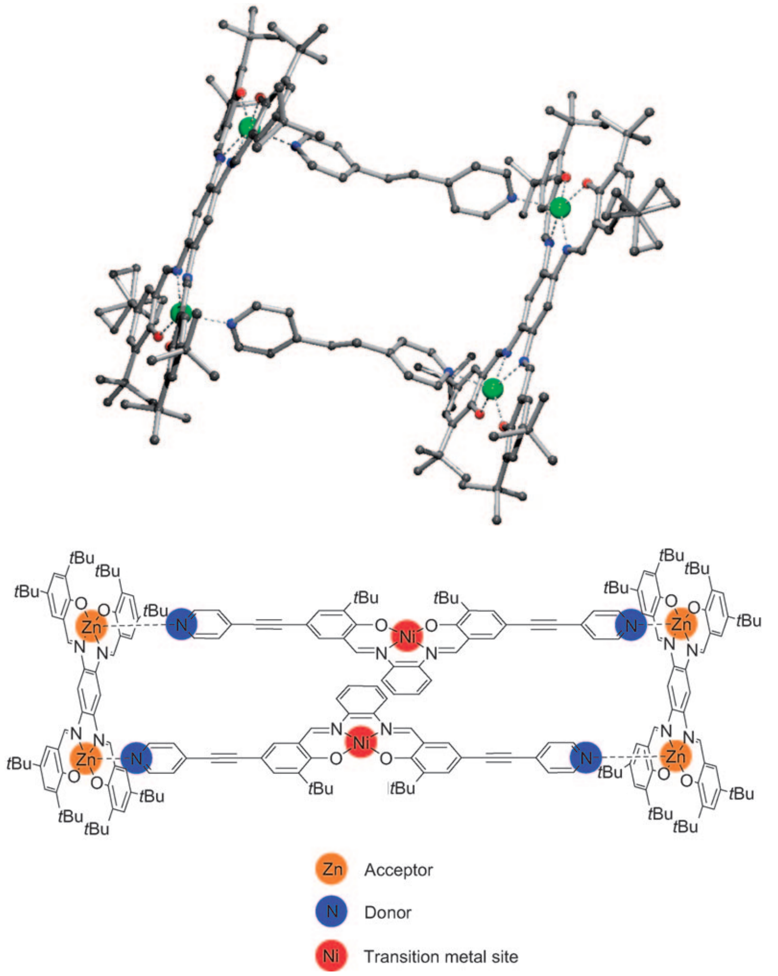
Templated Supra/Macromolecular Synthesis

Supramolecular chemistry is undoubtedly one of the leading disciplines in chemical sciences and may provide useful strategies for the construction of complicated architectures and new materials. Although metallosalen complexes have been known for many decades, only recently their convenient use as building blocks in supramolecular synthesis has been recognised.[24]

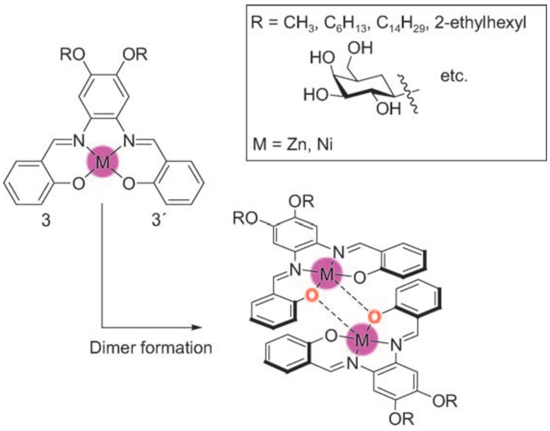
Salen compounds functionalised with pyridine side groups were reported by Hupp and co-workers.[25] These building blocks, combined with suitable Pt^{II} salts gave access to molecular loop/square structures through a directed assembly process (Scheme 10). When semi-flexible dipyridyl-functionalised salen ligands were employed, preferred formation and isolation of the loop structure was noted. The curvature that allows loop closure is facilitated by the backbone distortion of the bridging salen ligand, and likely entropic effects predominate in the assembly process. Reduction of the flexibility by metalation of the salen building block (M = Zn) and combination with the cationic Pt^{II} salt *or* post-metalation of the supramolecular loop system under appropriate conditions leads to exclusive and quantitative formation of the square-type structures. Introduction of various other metals into these supramolecular assemblies may lead to interesting new catalytic systems.

A similar approach toward supramolecular assembly formation by using pyridyl-containing salen scaffolds was undertaken by Kleij and Reek.[26] However, here the Zn^{II}-centred metallosalen complex was designed to have the N-donor atom within the bridging group between both imine fragments (Scheme 11). The relative disposition of the donor (pyridine-N atom) and acceptor sites (Zn metal centre) leads to directed formation of a macrocyclic, tetrameric supramolecular assembly. Such macrocycles are of broad current interest, and the first example of enantiomer separation using similar chiral structures has recently been reported.[27]

Templated approaches to various supramolecular structures using mono- and bis-Zn(salphen) complexes in conjunction with pyridine donors were reported by Kleij/Reek and co-workers. For instance, 4,4′-bipyridine bridged dimers[28] and box-shaped assemblies[29] arise from their combination with mono- or bis-Zn(salphen) building blocks. In the latter case, exclusive formation of the macrocyclic structure under dilute conditions was observed, both in solution and solid state phases (Scheme 12). A valuable exten-



Scheme 12. Examples of supramolecular assemblies based on pyridine donors and Zn(salphen) acceptors. Top: X-ray molecular structure of a box-shaped assembly using a flexible bis-pyridine ligand, the disorder for some *t*Bu groups is also shown. Bottom: schematic structure of a functional, heterotetrametallic salen-based supramolecular structure.



Scheme 13. Zn(salphen) complexes that are able to form metallogels and nanofibers.

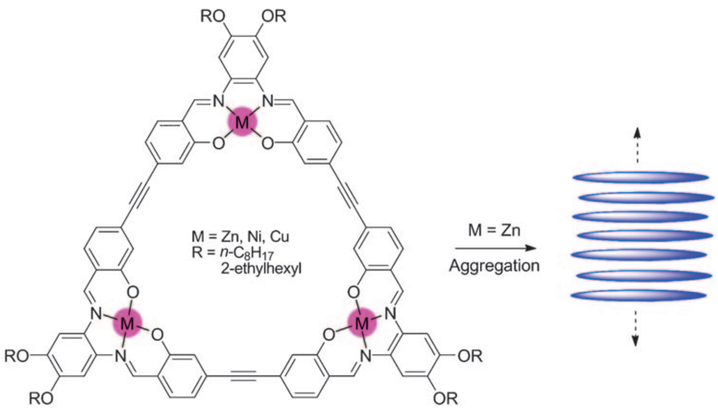
sion to this kind of box assemblies was communicated recently. The use of pyridyl-functionalised metallosalen complexes (Scheme 10) allows, through Zn–N_{pyr} coordinative motifs, the formation of templated macrocycles based on heterotetrametallic salen structures. Here, the two transition metal sites are in close proximity, thereby providing a way for cooperative catalytic operations upon introduction of appropriate metal ions in the metallosalen building block (Scheme 12).[30]

The Zn(salen) structure has also been exploited for the fabrication of other types of supramolecular architectures, including nanofibrils and nanotubes. MacLachlan reported the use of Zn(salphen) complexes that are able to assemble into metallogels and 1D nanofibres making use of Zn···O interactions (Scheme 13).[31] Insufficient steric bulk at the 3- and 3′-position allows dimerisation through μ_2-O bridging[23] and thus being the basis for the assembly process.

Gel formation was particularly observed in non-coordinating aromatic solvents, whereas no gel formation was observed in pyridine, DMF and MeCN. Moreover, TEM-analysis of these Zn(salphen) complexes showed nanofiber formation, principally ascribed to the Zn···O interactions and not to π–π stacking between the individual salphen complexes or hydrogen bonding. This assumption was supported by several additional experiments with a series of reference/model compounds. Upon changing the Zn for other metal ions (Ni, Cu, V), introduction of sterically demanding groups in the 3- and 3′-positions of the ligand (Scheme 13) or replacing the phenolic O atoms for S, no assembled fibrillar textures could be observed.

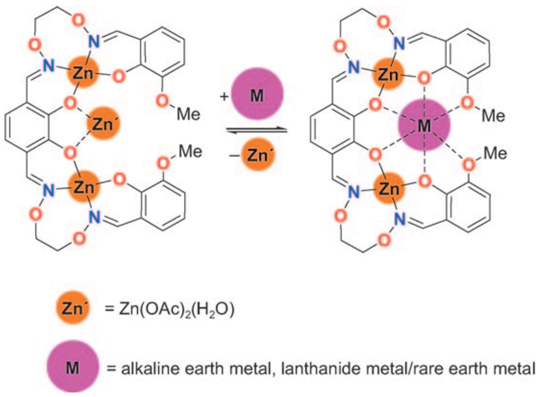
A similar approach toward the construction of aggregated, multimetallic macrocycles (Scheme 14) using Zn···O interactions was also investigated by the MacLachlan group.[32] Only in the case where M = Zn, aggregation was observed and spectroscopically characterised, and disruption of the assembly could be readily achieved by addition of suitable N-donor ligands. Interestingly, the aggregation process is accompanied by changes in the optical and fluorescent properties, a feature that may be used for chemical sensing purposes upon controlled de-aggregation using external ligands.

Specific and selective exchange of the central metal ion by (rare/alkaline) earth metal ions within trinuclear com-



Scheme 14. An assembled superstructure through Zn···O interactions using multimetallic salphen macrocycles.

plexes derived from oxime-based salen like systems was described by Nabeshima (Scheme 15).[33] The formation of the trinuclear Zn_3 complex affords a *C*-shaped compound with six O-atoms arranged in cyclic fashion useful for guest recognition. The size of the cavity that can wrap itself around appropriate guests directs the structure of the heterotrinuclear complex after Zn-for-M exchange, and different metallohelicenes with tuneable geometrical parameters were thus obtained depending on the type of guest metal ion.[33a,b] These helical frameworks may find use in various chiral recognition processes and/or catalytic procedures. An interesting example of a selective Ca^{2+} and Ba^{2+} receptor based on this site-selective transmetalation[34] has also been reported.[33c]



Scheme 15. Trinuclear oxime-based salen-like complexes and their site-selective mono-transmetalation leading to heterotrimetallic compounds.

Conclusion

From this overview it is evident that metallosalen scaffolds have become increasingly important in templated synthesis. A proper design of the salen-containing structure allows for precise control over the synthetic event, which would be virtually impossible to achieve without the use of the metallosalen scaffold. The metal zinc plays a crucial role for all forms of life and many important Zn-enzymes are known for their role as structural mediator or catalyst. Therefore, it is perhaps not completely surprising that Zn is found in the majority of the metallosalen structures that are capable of directing or templating structural/synthetic events. The Zn^{2+} ion has an extremely versatile coordination chemistry allowing, depending on the involved ligands, coordination numbers from 4 to 6 and geometries ranging from tetrahedral to square planar, square pyrimidal to trigonal bipyrimidal and even octahedral. This particular feature will probably maintain a prominent role in the design of new templated processes. Although a limited number of metallosalen templates have been reported, yet it can be concluded that exciting new developments may be expected in various applications that focus on structural and catalytic complexity. In our view, the metallosalen scaffold will undoubtedly continue to be a source of inspiration for many chemists.

Acknowledgements

AWK thanks the Institute of Chemical Research of Catalonia (ICIQ) and Institució Catalana de Recerca i Estudis Avançats (ICREA) for additional support.

---

[1] See for an excellent review on DNA-templated organic synthesis: X. Li, D. R. Liu, *Angew. Chem.* **2004**, *116*, 4956–4979; *Angew. Chem. Int. Ed.* **2004**, *43*, 4848–4870.

[2] For some reviews see: a) T. Katsuki, *Coord. Chem. Rev.* **1995**, *140*, 189–214; b) E. N. Jacobsen, *Acc. Chem. Res.* **2000**, *33*, 421–431; c) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410–421; d) J. F. Farlow, E. N. Jacobsen, *Top. Organomet. Chem.* **2004**, *6*, 123–152; e) E. M. McGarrigle, D. G. Gilheany, *Chem. Rev.* **2005**, *105*, 1563–1602. For simplicity, we here refer to salen as a general name for this kind of ligand structure, whereas in particular cases it will be emphasised which type of ligand was employed.

[3] a) W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, *J. Am. Chem. Soc.* **1990**, *112*, 2801–2803; b) R. Irie, K. Noda, Y. Ito, N. Matsumoto, T. Katsuki, *Tetrahedron Lett.* **1990**, *31*, 7345–7348.

[4] S. J. Wezenberg, A. W. Kleij, *Angew. Chem.* **2008**, *120*, 2388–2399; *Angew. Chem. Int. Ed.* **2008**, *47*, 2354–2364.

[5] a) A. W. Kleij, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Eur. J. Inorg. Chem.* **2005**, 4626–4634; b) S. Curreli, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *J. Org. Chem.* **2007**, *72*, 7018–7021.

[6] See for some recent examples: a) C. Mazet, E. N. Jacobsen, *Angew. Chem.* **2008**, *120*, 1786–1789; *Angew. Chem. Int. Ed.* **2008**, *47*, 1762–1765; b) T. Belser, E. N. Jacobsen, *Adv. Synth. Catal. Adv. Synth. Cat.* **2008**, *350*, 967–971; c) N. Madhavan, M. Weck, Adv. Synth. Cat. 2008, 350, 419–425.

[7] K. E. Splan, A. M. Massari, G. A. Morris, S.-Sheng Sun, E. Reina, S. T. Nguyen, J. T. Hupp, *Eur. J. Inorg. Chem.* **2003**, 2348–2351.

[8] See for some selected examples: a) G. H. Clever, K. Polborn, T. Carell, *Angew. Chem.* **2005**, *117*, 7370–7374; *Angew. Chem. Int. Ed.* **2005**, *44*, 7204–7208; b) G. H. Clever, Y. Söltl, H. Burks, W. Spahl, T. Carell, *Chem. Eur. J.* **2006**, *12*, 8708–8718; c) J. L. Czlapinski, T. L. Sheppard, *Chem. Commun.* **2004**, 2468–2469.

[9] E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 4256–4263.

[10] For a demonstrative example see: N. C. Gianneschi, P. A. Bertin, S. T. Nguyen, C. A. Mirkin, L. N. Zhakarov, A. L. Rheingold, *J. Am. Chem. Soc.* **2003**, *125*, 10508–10509.

[11] F. H. Zelder, J. Rebek Jr. , *Chem. Commun.* **2006**, 753–754.

[12] M. Kuil, P. E. Goudriaan, P. W. N. M. Van Leeuwen, J. N. H. Reek, *Chem. Commun.* **2006**, 4679–4681.

[13] M. Kuil, P. E. Goudriaan, A. W. Kleij, D. M. Tooke, A. L. Spek, P. W. N. M. van Leeuwen, J. N. H. Reek, *Dalton Trans.* **2007**, 2311–2320.

[14] See for example: a) J. K.-H. Hui, M. J. MacLachlan, *Chem. Commun.* **2006**, 2480–2482; b) P. D. Frischmann, J. Jiang, J. K.-H. Hui, J. J. Grzybowski, M. J. MacLachlan, *Org. Lett.* **2008**, *10*, 1255–1258; c) C. Ma, A. Lo, A. Abdolmaleki, M. J. MacLachlan, *Org. Lett.* **2004**, *6*, 3841–3844; d) T. Nabeshima, H. Miyazaki, A. Iwasaki, S. Akine, T. Saiki, C. Ikeda, *Tetrahedron* **2007**, *63*, 3328–3333; e) S. Akine, D. Hashimoto, T. Saiki, T. Nabeshima, *Tetrahedron Lett.* **2004**, *45*, 4225–4227.

[15] A. J. Gallant, M. J. MacLachlan, *Angew. Chem.* **2003**, *115*, 5465–5468; *Angew. Chem. Int. Ed.* **2003**, *42*, 5307–5310.

[16] S. Akine, S. Kagiyama, T. Nabeshima, *Inorg. Chem.* **2007**, *46*, 9525–9527.

[17] For some demonstrating examples of the use of oxime-based salen-type derivatives in inorganic synthesis see: a) S. Akine, T. Taniguchi, T. Nabeshima, *Inorg. Chem.* **2004**, *43*, 6142–6144; b) S. Akine, W. Dong, T. Nabeshima, *Inorg. Chem.* **2006**, *45*, 4677–4684.

[18] S. Akine, S. Sunaga, T. Taniguchi, H. Miyazaki, T. Nabeshima, *Inorg. Chem.* **2007**, *46*, 2959–2961.

[19] a) P. D. Frischmann, A. J. Gallant, J. H. Chong, M. J. MacLachlan, *Inorg. Chem.* **2008**, *47*, 101–112; b) A. J. Gallant, J. H. Chong, M. J. MacLachlan, *Inorg. Chem.* **2006**, *45*, 5248–5250.

[20] G. Parkin, *Chem. Rev.* **2004**, *104*, 699–767.

[21] H. Koyama, Y. Saito, *Bull. Chem. Soc. Jpn.* **1954**, *27*, 112–114.

[22] E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 410–412.

[23] These dimeric Zn(salphen) complexes are formed through μ_2-O bridging and dimerisation occurs for those complexes that lack sufficient steric bulk in the respective 3- and 3′-positions of the phenyl side groups of the salen ligand.

[24] For one of the early examples see: K. Chichak, U. Jacquemard, N. Branda, *Eur. J. Inorg. Chem.* **2002**, 357–368.

[25] S.-S. Sun, C. L. Stern, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2004**, *126*, 6314–6326.

[26] A. W. Kleij, M. Kuil, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Inorg. Chem.* **2007**, *46*, 5829–5831.

[27] G. Li, W. Yu, J. Ni, T. Liu, Y. Liu, E. Sheng, Y. Cui, *Angew. Chem.* **2008**, *120*, 1265–1269; *Angew. Chem. Int. Ed.* **2008**, *47*, 1245–1249.

[28] A. W. Kleij, M. Kuil, M. Lutz, D. M. Tooke, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leeuwen, J. N. H. Reek, *Inorg. Chim. Acta* **2005**, *359*, 1807–1814.

[29] a) A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743–4750. For recently published similar bis-Zn(salphen) supramolecular building blocks see: b) S. Curreli, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Eur. J. Inorg. Chem.* **2008**, 2863–2873.

[30] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 2925–2927.

[31] J. K.-H. Hui, Z. Yu, M. J. MacLachlan, *Angew. Chem.* **2007**, *119*, 8126–8129; *Angew. Chem. Int. Ed.* **2007**, *46*, 7980–7983.

[32] C. T. L. Ma, M. J. MacLachlan, *Angew. Chem.* **2005**, *117*, 4250–4254; *Angew. Chem. Int. Ed.* **2005**, *44*, 4178–4182.

[33] a) S. Akine, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2006**, *128*, 15765–15774; b) S. Akine, T. Taniguchi, T. Nabeshima, *Angew. Chem.* **2002**, *114*, 4864–4867; *Angew. Chem. Int. Ed.* **2002**, *41*, 4670–4673; c) S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima. *J. Am. Chem. Soc.* **2005**, *127*, 540–541.

[34] For a related transmetalation of Zn(salphen) complexes see: a) E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2007**, *46*, 7265–7267; b) S. J. Wezenberg, G. A. Metselaar, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chim. Acta* **2008**, DOI: 10.1016/j.ica.200805022.