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# Modular Synthesis of Heterobimetallic Salen Structures Using Metal Template

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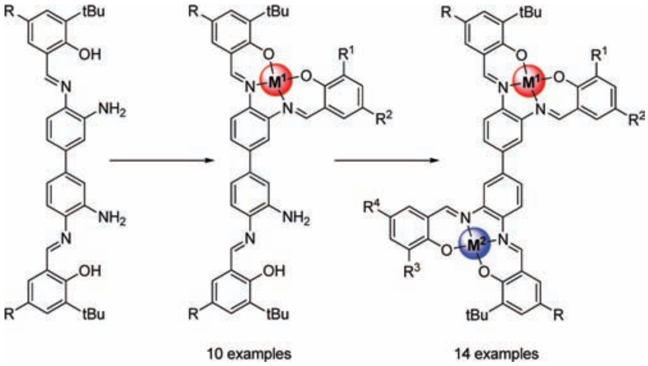
## ABSTRACT



**A modular and general synthetic method is disclosed for nonsymmetrical heterobimetallic bis-salphen structures starting from a series of synthetically convenient monometalated triimine precursors. This methodology permits the introduction of various combinations of metal ions within the bis-salphen framework potentially useful in multifunctional materials.**

The salen ligand is an excellent scaffold for the coordination of many different types of metal ions.[1] To date, their primary application has been homogeneous catalysis, although recently, the focus has expanded to the use of (metallo)salen building blocks for other types of applications and materials[2] including (cooperative) multimetallic catalysis,[3] supramolecular materials,[4] and molecular sensors.[5] Another interesting development is the design and use of multimetallosalen structures in which the individual salen fragments are (non)covalently connected via a suitable spacer unit or to a polymer matrix.[6] Jacobsen and co-workers have recently demonstrated that bimetallic salens[7] based on covalent

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structures are excellent candidates for cooperative homogeneous catalysis operations.[8] However, the covalent multistep approach for most known systems toward bimetallic catalysts based on salen ligands could limit fine-tuning of the catalyst properties by variation of the peripheral substituents. Furthermore, these reported procedures lack the option to access heterometallic structures in a controlled fashion. Heteromultimetallic complexes comprising metal ions displaying distinct substrate affinity behavior may lead to new application potential in cascade processes or multifunctional catalysts focusing on dual activation.[9]

We have become increasingly interested in the construction of bimetallic bis-salphen complexes based on the 3,3′-diaminobenzidene backbone. Previously, we reported on the modular synthesis of *homo*bimetallic synthons that display a nonsymmetry within each salen unit.[10] The simple introduction of different functionalities in the phenyl side groups of the salen unit could be accomplished using a stepwise approach starting from diimine precursors **A** and **B** (Scheme 1, at the right). We therefore anticipated that the 3,3′-diaminobenzidene would also be a good starting point for the construction of heterobimetallic salphen-based structures using metal templation as means toward selective construction of both salphen units. Here we report the modular synthesis of heterobimetallic salphen structures with various metal ion combinations using versatile monometallic triimine intermediates.

The synthesis of monometallic triimine complexes **1**−**10** (Scheme 1) was first probed under dilute conditions using diimines **A** and **B**, various salicylaldehydes, and $Zn(OAc)_2 \cdot 2H_2O$ as starting materials.[10c] This initial screening stage provided useful information for the preferred reaction conditions and reagents (see Supporting Information). Hereafter, other combinations of substituted salicylaldehydes and metal acetate reagents were used under comparable experimental conditions (Scheme 1 and Table 1). The introduction of different metal ions could be accomplished, and their structures were fully confirmed by a range of analytical techniques (Supporting Information).

**Scheme 1.** Synthesis of Monometallic Triimine Synthons **1**−**10**

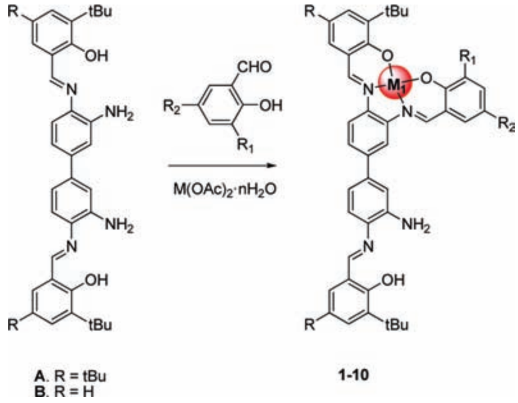

**Table 1.** Synthesis of Monometallic Triimine Precursors **1**−**10** Starting from Diimines **A** and **B**[a]

| complex | $M_1$ | R | $R_1$ | $R_2$ | yield (%)[b] |
|---|---|---|---|---|---|
| **1** | Zn | $^t$Bu | $NO_2$ | $NO_2$ | 60 |
| **2** | Zn | H | $NO_2$ | $NO_2$ | 65 |
| **3** | Zn | H | Cl | Cl | 64 |
| **4** | Zn | H | H | Br | 74 |
| **5** | Ni | $^t$Bu | $NO_2$ | $NO_2$ | 69 |
| **6** | Ni | $^t$Bu | Cl | Cl | 54 |
| **7** | Ni | H | $NO_2$ | $NO_2$ | 69 |
| **8**[c] | Pd | H | $NO_2$ | $NO_2$ | 50 |
| **9**[c] | Pd | $^t$Bu | Cl | Cl | 40 |
| **10** | Mn | $^t$Bu | $NO_2$ | $NO_2$ | 27 |

[a] Reactions were carried out in $CHCl_3$/MeOH at rt using 1 equiv of salicylaldehyde and 1 equiv of metal precursor. [b] Isolated yield. [c] Reaction performed in THF/MeOH.

Table 1 shows that the synthesis of these monometallic triimine structures has a reasonable scope in terms of metal ion and peripheral substituents. In view of the potential risk of formation of bimetallic bis-salen complexes, the isolated yields of pure monometallic species in the majority of the reactions are good. Such a selectivity is generally very difficult to achieve in multisalen structures because scrambling of imine units may occur, resulting in inseparable mixtures. The formation of the monometallic compounds **1**−**10** is easily monitored by $^1$H NMR (DMSO-$d_6$). Whereas the diimines **A** and **B** only display a single peak for the imine protons, complexes **1**−**10** give rise to the presence of three distinct CH═N resonances in a 1:1:1 integral ratio consistent with their molecular asymmetry (Figure S1 in Supporting Information). MALDI-TOF-MS further confirmed the presence of monometalated structures. The unusual structure of complex **1** could also be confirmed by X-ray crystallography (Figure 1).

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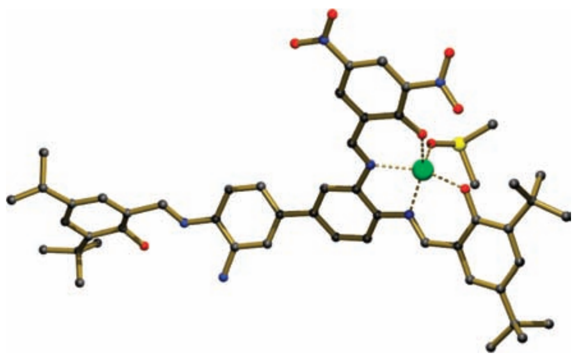

**Figure 1.** X-ray molecular structure for **1·DMSO**. Hydrogen atoms and co-crystallized solvent molecules are omitted for clarity. Color codes: Zn = green, N = blue, O = red, S = yellow, C = dark gray.

Our approach toward heterobimetallic salphen structures makes direct use of monometallic synthons **1**−**10** (Scheme 2). Imine formation in the presence of a (substituted) salicylaldehyde and a (second) templating metal precursor should allow selective formation of the second metallosalphen unit. The synthesis of heterobimetallic complexes **11**−**24** was then carried out using a general protocol (Supporting Information), and Table 2 summarizes the results. For complexes **11**−**16**, the mono-Ni triimine precursors were used as a starting point, and various other metal ions (cf., $M_2$) and substituents ($R_3$ and $R_4$) could be easily introduced. Complex **13** represents a useful example within this series of derivatives as it contains a chiral binaphthyl unit useful in catalytic processes.[11] The Pd−Ni and Pd−Zn heterobimetallics **19**−**22** were produced from mono-Pd triimine precursors **8** and **9**, whereas the mono-Zn triimine precursor **2** could be converted into the bis-metallosalphen complexes **23** and **24**. These latter two examples are somewhat remarkable in terms of the kinetic stability of the Zn(salphen) module within **2**. This unit has been shown to be prone to transmetalation by various metal acetate salts.[12] For instance, when **2** is treated with $Ni(OAc)_2$•$4H_2O$ in the presence of a substituted salicylaldehyde, mixtures of compounds are detected both by $^1$H NMR as well as MALDI-TOF-MS. These mixtures are a result of the (partial) transmetalation of the Zn(salphen) module and (partial) metalation of the half-salen site.

**Scheme 2.** Synthesis of Heterobimetallic Complexes **11**−**24**

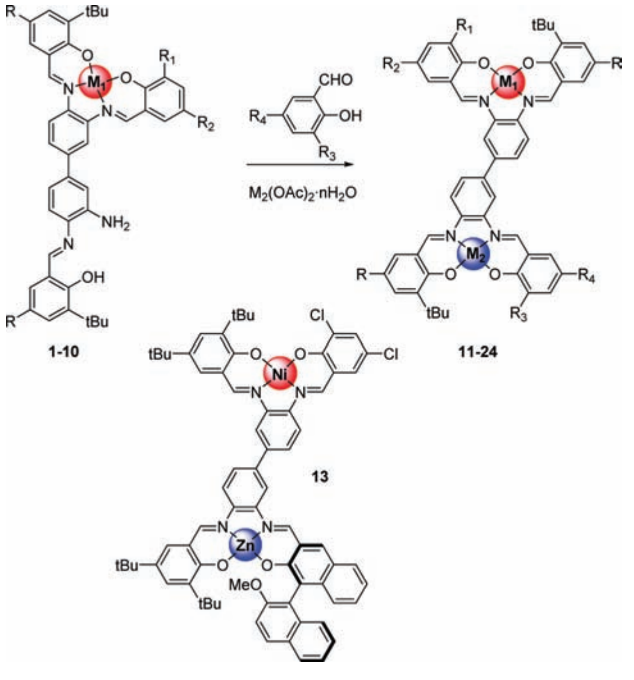

**Table 2.** Synthesis of Heterobimetallic Complexes **11**−**24** Using Monometalated Triimine Complexes **1**−**10**[a]

| complex | $M_1$ | $M_2$ | R | $R_1$ | $R_2$ | $R_3$ | $R_4$ | yield (%)[b] |
|---|---|---|---|---|---|---|---|---|
| **11** | Ni | Zn | $^t$Bu | $NO_2$ | $NO_2$ | $NO_2$ | $NO_2$ | 85 |
| **12** | Ni | Zn | $^t$Bu | Cl | Cl | Br | H | 88 |
| **13** | Ni | Zn | $^t$Bu | Cl | Cl | [c] | [c] | 84 |
| **14** | Ni | Zn | $^t$Bu | Cl | Cl | $^t$Bu | $^t$Bu | 72 |
| **15** | Ni | Mn | $^t$Bu | Cl | Cl | $NO_2$ | $NO_2$ | 36 |
| **16** | Ni | Cu | $^t$Bu | Cl | Cl | allyl | H | 84 |
| **17** | Ni | Pd | $^t$Bu | $NO_2$ | $NO_2$ | Cl | Cl | 54[d] |
| **18** | Ni | Pd | $^t$Bu | Cl | Cl | Cl | Cl | 79 |
| **19** | Pd | Ni | H | $NO_2$ | $NO_2$ | Cl | Cl | 90 |
| **20** | Pd | Ni | H | $NO_2$ | $NO_2$ | $^t$Bu | H | 80 |
| **21** | Pd | Ni | $^t$Bu | Cl | Cl | $^t$Bu | $^t$Bu | 76 |
| **22** | Pd | Zn | H | $NO_2$ | $NO_2$ | Br | H | 71 |
| **23** | Zn | Pd | $^t$Bu | $NO_2$ | $NO_2$ | Cl | Cl | 52[d] |
| **24** | Zn | Cu | $^t$Bu | $NO_2$ | $NO_2$ | Cl | Cl | 66 |

[a] Reactions were carried out in $CHCl_3$/MeOH, THF, or THF/MeOH at rt. [b] Isolated yield of pure materials. [c] (*S*)-2-Hydroxy-2′-methoxy-1,1′-binaphthyl-3-carbaldehyde was used as reagent. [d] After recrystallization.

This hampered the isolation of the pure heterobimetallic Zn−Ni complex. However, in the case of **23** and **24**, we found that the metalation of the half-salen unit proceeds rather selectively, providing crude products containing the desired heterobimetallic complex as the major component. Pure **23**, as revealed by $^1$H NMR, was obtained by a single recrystallization in 52% yield, while for paramagnetic **24**, an alternative, confirmative analysis for its proposed structure had to be carried out.

As for the monometallic triimine complexes, the formation of the (nonsymmetrical) heterobimetallic species could be easiliy substantiated by NMR and MALDI-TOF mass spectrometry. The $^1$H and $^{13}C\{^1H\}$ NMR spectra show four distinct peaks for the imine-H/imine-C (see Figure S1 in Supporting Information for examples).

For heterobimetallic complex **17**, suitable crystals could be obtained for X-ray diffraction (Figure 2) and unambiguously revealed its molecular structure. To our knowlegde, this is the first example of a structurally characterized heterobimetallic bis-salen complex.

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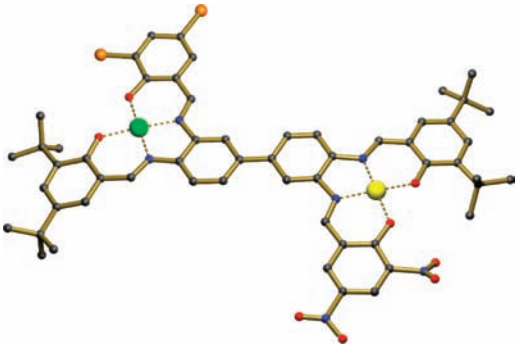

**Figure 2.** X-ray molecular structure for **17**. Hydrogen atoms and co-crystallized solvent are omitted for clarity. Color codes: Ni = green, Pd = yellow, Cl = orange, N = blue, O = red, C = dark gray.

MALDI-TOF-MS analysis of **24** supported the formation of a single heterobimetallic Zn−Cu species but could not rule out the possibility of having mixtures containing the desired species and the isomeric Cu−Zn complex that results from transmetalation of the Zn(salphen) site in **2** and metalation of the half-salen site by in situ formed Zn(OAc)$_2$. We therefore decided to prepare four reference complexes (**25**−**28**, Figure 3) that resemble the four possible metallosalphen units that can be present after treatment of **2** by Cu(OAc)$_2$. The UV−vis spectra of **24**−**28** were recorded in CHCl$_3$, and the spectrum of heterobimetallic **24** was compared with the individual complexes **25**−**28** and also with 1:1 mixtures of **25**+**28** and **26**+**27** (Figure 3). From this comparison, it can be deduced that the UV−vis data for **24** show the largest resemblance with the 1:1 combination of **25**+**28**, and therefore, it may be concluded that the proposed structure for **24** is correct. This is also in line with the selective incorporation of Pd into **1**, which gave heterobimetallic **23**.

In summary, we here present a modular synthetic strategy for the formation of heterobimetallic salphen complexes that utilizes synthetically readily accessible monometallic triimine precursors. The presence of two different complexed metal ions could be useful in the creation of multifunctional materials where both metal ions display different though complementing functions such as in the case of a recognition and catalytic site. To our knowledge, a straightforward and selective method for preparation of heteromultimetallic salen structures is unprecedented and could have great potential in the field of homogeneous catalysis and particularly in cascade or tandem processes. Currently, we are focusing on the preparation of other heteromultimetallic bis-salen structures and their application in (supramolecular) catalysis.

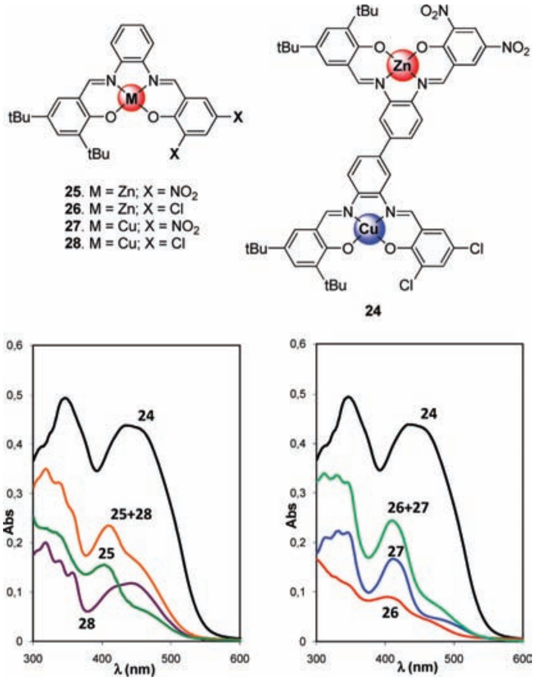

**Figure 3.** UV−vis analysis/comparison (CHCl$_3$) between heterobimetallic complex **24** and reference complexes **25**−**28**.

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**Supporting Information Available:** Data for all new compounds and copies of relevant spectra, further crystallographic comments, and crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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