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Templated Synthesis and Site-Selective Conversion of Completely Nonsymmetrical Bis-Metallosalphen Complexes

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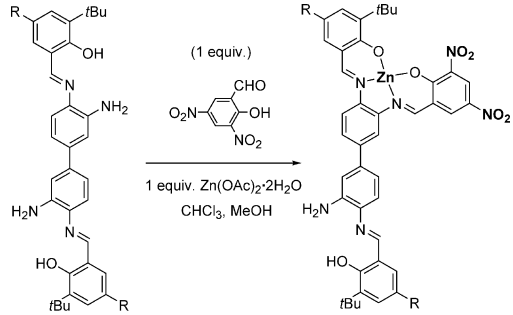
A metal-templated, stepwise approach toward fully nonsymmetrical bis-metallosalphen complexes is described. The synthesis comprises the selective monometalation of diimine precursors and subsequent introduction of the second metal ion by using various salicylaldehyde reagents. In the case of a bis-Zn(salen) derivative, the presence of different peripheral substituents on the two metallosalen units gave rise to a large difference in kinetic stability, which was used to selectively demetalate the more labile site. This result shows promise for the preparation of heterobimetallic structures. The first X-ray molecular structure of a completely nonsymmetrical bis-salphen complex is also reported.

Introduction

Salen ligands are generally considered privileged, because many stereoselective transformations can be carried out with these versatile structures.[1] Recently, the use of (multimetallic) metallosalen complexes in material chemistry has emerged as a powerful approach towards functional (supramolecular) systems with wide-ranging properties.[2,3] Although synthetic salen chemistry has matured significantly over the last decade,[4] the development of procedures for multinuclear salen complexes that allow particular control over the properties of each individual complexed metal ion still represents a great challenge,[5] as a consequence of the labile nature of the imine bond during synthesis. The presence of different metallosalen units within the multinuclear complex can provide a means for site-selective functionalization that is potentially interesting for the development of heteromultimetallic systems[6] useful in cascade or orthogonal tandem catalysis. We recently reported on the preparation of a small library of diimine precursors derived from 3,3′-diaminobenzidine (see Scheme 1 for an example) and their conversion into symmetrical bimetallic salphen complexes with a nonsymmetry within each salen unit.[7,8] We anticipated that a selective introduction of one metallosalen module onto the diaminobenzidene backbone could lead to an interesting monometallic triimine precursor, whose unreacted half-salen unit[7] subsequently tolerates the introduction of different aryl substituents in the second salen unit. Here we report the Zn-templated synthesis of a unique monometallic precursor and its conversion into fully nonsymmetrical bis-metallosalphen complexes [salphen = *N*,*N*′-1,2-phenylenebis(salicylideneimine)]. The presence of different peripheral substituents on both Zn(salphen) modules creates a significant difference in the kinetic stability of the Zn ions, which is demonstrated by a site-selective demetalation of one of the Zn(salphen) units.



A: R = *t*Bu
B: R = H

1: R = *t*Bu
2: R = H

Scheme 1. Synthesis of monometallic triimine precursors **1** and **2**.

Results and Discussion

We recently reported the preparation of a series of diimines, including **A** and **B** (Scheme 1), derived from 3,3′-diaminobenzidine.[7,8] These diimines can be prepared on a larger scale and serve as valuable intermediates for symmetrical homobimetallic salphen complexes. We anticipated that, under appropriate conditions, these diimines could

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also serve to access monometalated precursors comprising one metallosalen unit and a (unreacted) half-salen unit at the other end of the benzidene backbone. Different solvents, reagents and conditions were initially screened for selective formation of monometalated structures. Under diluted conditions and by using stoichiometric amounts of both 3,5-dinitrosalicylaldehyde and $Zn(OAc)_2 \cdot 2H_2O$, we found that mono-Zn complexes **1**–**2** could be readily obtained in moderate to good yields (40–80%) in repeated experiments. Upon using either higher concentrations or other reaction stoichiometries, mixtures of components were obtained (i.e. unreacted diimine and mono- as well as bimetallic structures), which complicated compound purification.

The identity of mono-Zn compounds **1** and **2** can be easily deduced from their respective ^1H NMR and $^{13}C\{^1H\}$ NMR spectra. While diimines **A** and **B** produce only a single imine resonance, compound **1** and **2** give rise to three separate imine peaks consistent with the nonsymmetric nature of these structures (Figure 1). Further analytical proof for the structures of these compounds was provided by MALDI-TOF mass spectrometry.

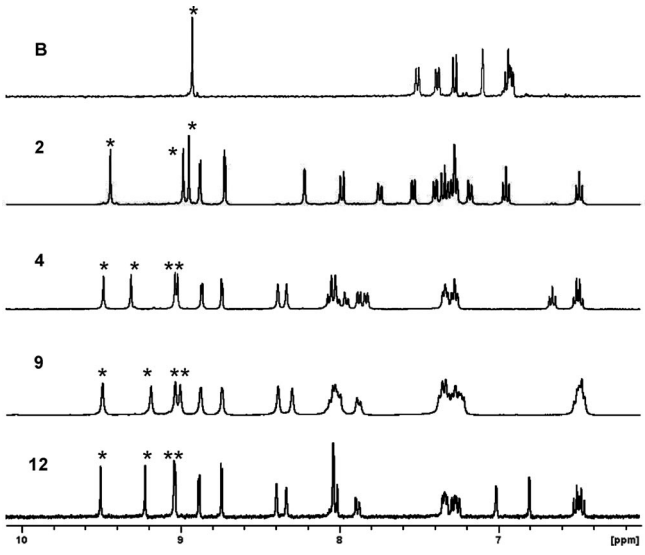
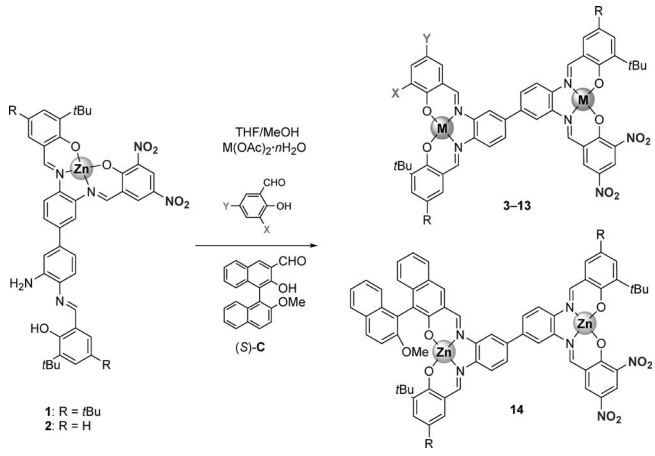


Figure 1. Comparison between the aromatic regions (^1H NMR, [D_6]DMSO) of compounds **B**, **2**, **4**, **9** and **12**. The imine protons in each compound are marked with an asterisk.

Mono-Zn complexes **1** and **2** were then used as starting materials for synthesizing completely dissymmetric bimetallic salphen structures (Table 1 and accompanying Figure). Combination of **2** with various salicylaldehydes and $Zn(OAc)_2 \cdot 2H_2O$ in THF/MeOH provided a synthetic route to homobimetallic compounds with ample scope. In all cases, the second metalation reaction is fast enough to prevent potential imine hydrolysis and/or equilibration of the half-salen unit.[9] Thus, it is fair to say that the metal ions function as templating centres for the construction of both the mono-Zn precursors **1** and **2**, as well as complexes **3**–**14** (Table 1).

Table 1. Synthesis of various fully nonsymmetrical homobimetallic salphen complexes by using the monometallic synthons **1** and **2**.[a]



Complex	M	R	X	Y	Yield [%][b]
3	Zn	H	Cl	Cl	92
4	Zn	H	NO_2	H	83
5	Zn	H	Br	H	82
6	Zn	H	*t*Bu	Br	68
7	Zn	H	H	Br	90
8	Zn	H	allyl[c]	H	59[d]
9	Zn	H	Me	H	67
10	Zn	H	H	H	81
11	Zn	H	*t*Bu	H	76
12	Zn	H	OMe	allyl[c]	76
13	Ni	H	*t*Bu	H	68
14	Zn	*t*Bu	[e]	[e]	41

[a] Reactions were performed in THF/MeOH (4:1 v/v) at room temp. [b] Isolated yield. [c] allyl: $-CH_2CH{=}CH_2$. [d] After recrystallization from DMSO/Et_2O. [e] See the scheme at the top of the table.

Interestingly, both polar as well as nonpolar substituents may be readily introduced on the periphery of the metallosalen unit in the second metalation step. The presence of nonpolar groups renders the complex more soluble, and isolated yields in these cases are, as a consequence, lower. Mono-Zn complex **2** could also be directly converted into bis-Ni(salphen) derivative **13** by using an excess of $Ni(OAc)_2 \cdot 4H_2O$ and 3-*tert*-butylsalicylaldehyde in the second metalation stage. Here, the reaction sequence involves a transmetalation of the Zn(salphen) unit[10] and completion of the half-salen unit with subsequent metalation by the Ni reagent. This latter example demonstrates that various nonsymmetrical bis-metallosalphen can be accessed by using mono-Zn precursors **1** and **2**. As for mono-Zn complexes **1** and **2**, the nonsymmetrical nature of bimetallic species **3**–**14** is revealed in their NMR spectra by the presence of four distinct peaks for the imine protons/carbons (Figure 1).

Finally, we also examined the possibility of introducing chirality in these nonsymmetrical homobimetallic structures. Chiral binaphthyl derivative (*S*)-**C** (Table 1, Figure) [11] was utilized to prepare chiral bis-Zn(salphen) complex **14**. Although the isolated (non-optimized) yield was only moderate (Table 1), this result yet further illustrates the versatility of the presented approach toward nonsymmetrical

bimetallic salphen structures and their potential use in asymmetric synthesis.

Single crystals of complex **12** were obtained from THF/MeOH and analyzed by X-ray diffraction (Figure 2). The structure shows unambiguously the molecular nonsymmetry: one Zn(salphen) unit carries an allyl substituent at the 5-position. This allyl fragment may be of great use in subsequent synthetic operations in order to arrive at larger multinuclear salen structures through olefin metathesis reactions.

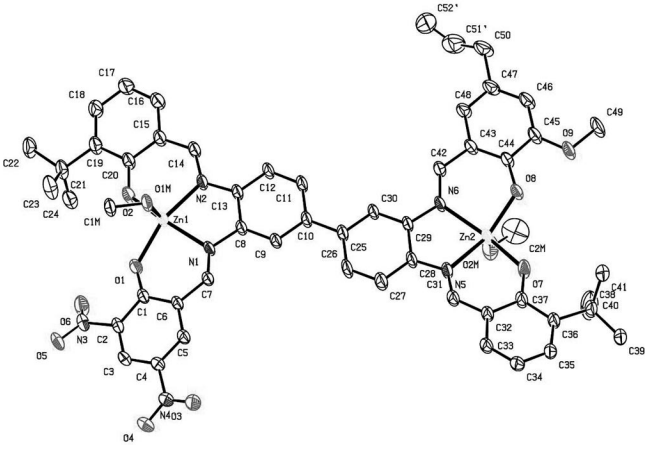
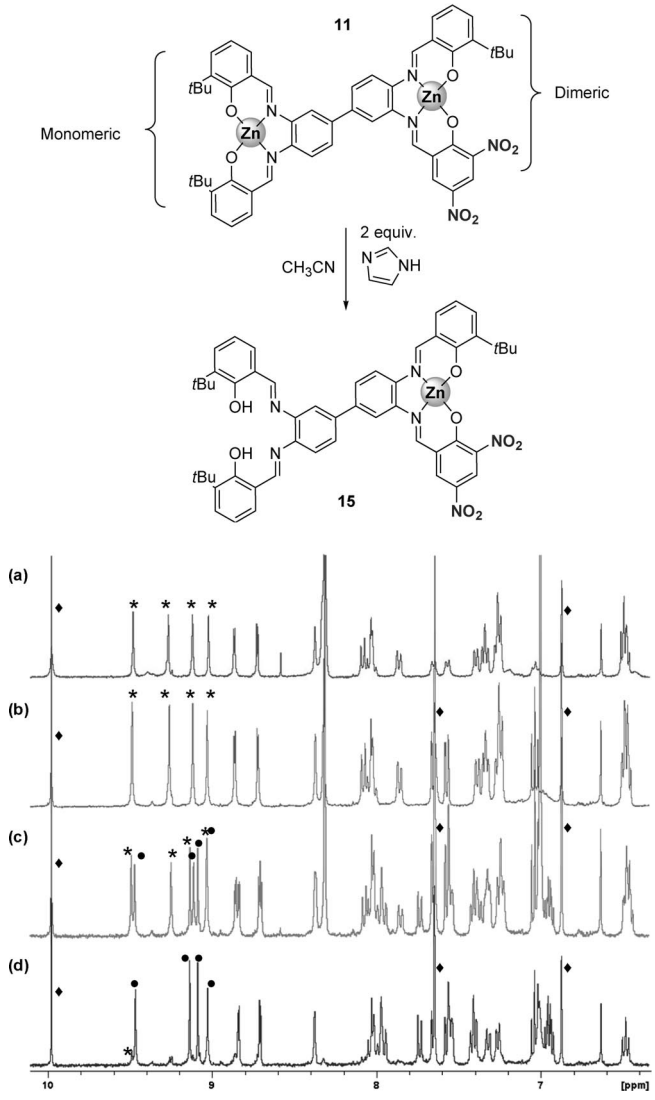


Figure 2. X-ray molecular structure of complex **12** with two axially coordinating MeOH ligands. Co-crystallized solvent molecules, H-atoms and disorder in one of the MeOH ligands, one of the NO_2 groups and the allyl group are omitted for clarity.

Complex **11** constitutes an interesting combination of two distinct Zn(salphen) modules. One of the Zn(salphen) units has sterically demanding *tert*-butyl groups at the 3 and 3′ positions: the presence of these *tert*-butyl groups is generally considered necessary to prevent dimerization of the Zn(salphen) complex through bridging of one of the oxygen atoms of the N_2O_2 donor set.[12–14] We recently reported that such monomeric Zn(salphen) complexes are susceptible to decomposition in (aqueous) noncoordinating solvents[15] and in the presence of protic N-heterocyclic ligands.[16] We therefore probed the selective demetalation of complex **11**,[17,18] having both a dimeric as well as monomeric site (Scheme 2), in a noncoordinating medium. Stirring of a sample of **11** in aqueous $CHCl_3$, however, did not gave a selective demetalation of the structure, as illustrated by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry. Treatment of **11** with two equivalents of imidazole[16] in CH_3CN proved to be more successful. In due course, the monomeric site was demetalated with a calculated 85% conversion [Scheme 2, spectrum (d)] and a remarkably high selectivity, providing a clean route towards monometalated bis-salphen structure **15** (see Scheme 2). The formation of **15** could be substantiated by the presence of a diagnostic imine peak at 9.5 ppm and the presence of a set of two distinct OH resonances located around 14.1 ppm (see also Supporting Information). This result demonstrates that the two Zn(salphen) units in **11** possess a significantly different kinetic stability under the experimental conditions. Obviously, the nonmetalated site in **15** could provide a means to access useful heterobimetallic structures.[19]



Scheme 2. Site-selective conversion of nonsymmetrical bis-Zn(salphen) complex **11** into monometalated **15** by using imidazole; below the NMR spectra ([D_6]DMSO) following this conversion: (a) t = 0 h, 1.1 equiv. imidazole, (b) t = 4 h, 1 equiv. imidazole, (c) t = 2 h, 2.1 equiv. imidazole, (d) t = 20 h, 2.1 equiv. imidazole; * = imine resonances of complex **11**, ● = imine resonances of complex **15**, ♦ = imidazole resonances.

Conclusions

In summary, we present here the first stepwise and selective approach toward the construction of fully nonsymmetrical bis-metallosalphen complexes with ample peripheral functionalization. The key intermediates, i.e. monometalated triimine precursors **1** and **2**, are prepared by a metal-templated approach. The Zn ions in these complexes serve to stabilize the salphen unit and prevent imine hydrolysis/equilibration. In the second metalation step, again metal

templation facilitates selective formation of nonsymmetrical derivatives **3**–**14**. As an illustrative example, bis-Zn(salphen) complex **11** has been used to take advantage over the significant difference in kinetic stability between the monomeric and dimeric Zn(salphen) sites, which leads, under appropriate conditions, to site-selective monodemetalation. This observation may be considered a useful starting point for the formation of heterobimetallic derivatives that may find application in homogeneous catalysis. Currently, we are exploring the utilization of our methodology for bimetallic salen complexes valuable in catalytic applications.

Experimental Section

Mono-Zn(salphen) Complex 2: To a solution of diimine **B** (181.8 mg, 0.340 mmol) in $CHCl_3$ (120 mL) was added subsequently a solution of 3,5-dinitrosalicylaldehyde (74.3 mg, 0.350 mmol) in MeOH (10 mL) and a solution of $Zn(OAc)_2{\cdot}2H_2O$ (74.9 mg, 0.341 mmol) in MeOH (10 mL). The colour of the homogeneous mixture first turned deep orange/red and then yellow (after addition of the Zn reagent). The mixture was stirred at room temp. for 18 h and was then filtered to furnish a red solid (Fraction 1: 115.6 mg, 43%). A second fraction was obtained by concentration of the mother liquors and trituration of the residue with MeOH and filtration. The second fraction was recrystallized from THF/MeOH to finally yield the pure product (red solid, 58.6 mg). Total yield: 174.2 mg (0.220 mmol, 65%). ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 13.93 (s, 1 H, OH), 9.45 (s, 1 H, CH=N), 8.99 (s, 1 H, CH=N), 8.96 (s, 1 H, CH=N), 8.88 (d, ^4J = 3.1 Hz, 1 H, ArH), 8.72 (d, ^4J = 3.1 Hz, 1 H, ArH), 8.23 (d, ^4J = 1.5 Hz, 1 H, ArH), 7.99 (d, ^3J = 8.7 Hz, 1 H, ArH), 7.75 (d, ^3J = 8.6, ^4J = 1.6 Hz, 1 H, ArH), 7.53 (d, ^3J = 7.8, ^4J = 1.4 Hz, 1 H, ArH), 7.40 (d, ^3J = 7.8 Hz, 1 H, ArH), 7.35 (d, ^3J = 8.3 Hz, 1 H, ArH), 7.30 (d, ^3J = 8.0 Hz, 1 H, ArH), 7.26–7.28 (m, 2 H, ArH), 7.18 (d, ^3J = 8.2, ^4J = 1.8 Hz, 1 H, ArH), 6.95 (t, ^3J = 7.7 Hz, 1 H, ArH), 6.49 (t, ^3J = 7.5 Hz, 1 H, ArH), 5.21 (s, 2 H, NH2), 1.464 [s, 9 H, C(CH$_3$)$_3$], 1.456 [s, 9 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]-DMSO): δ = 172.06, 166.95, 163.57, 162.50, 161.91, 159.46, 142.90, 142.38, 141.60, 139.45, 138.90, 138.52, 138.43, 136.39, 135.81, 134.69, 133.63, 131.65, 131.10, 130.91, 127.00, 123.91, 122.57, 119.48, 119.44, 119.11, 118.48, 117.30, 115.68, 114.90, 113.45, 112.75, 34.90, 34.49, 29.53, 29.26 ppm. MS (MALDI+, pyrene): *m*/*z* = 775.2 [M – CH$_3$]$^+$, 791.1 [M + H]$^+$, 797.2 [M + Li]$^+$, 813.2 [M + Na]$^+$. $C_{41}H_{38}N_6O_7Zn$ (792.19): calcd. C 62.16, H 10.61, N 4.83; found C 61.98, H 10.83, N 5.05.

Bis-Zn(salphen) Complex 6: To a solution of mono-Zn complex **2** (41.5 mg, 0.0524 mmol) and 5-bromo-3-*tert*-butylsalicylaldehyde (29.0 mg, 0.113 mmol) in THF (30 mL) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (28.8 mg, 0.131 mmol) in MeOH (10 mL) The reaction mixture was stirred for 18 h at room temp. Then, the solvent was removed under reduced pressure, and the residue was triturated with MeOH (10 mL) and filtered. The orange solid product was further air-dried. Yield: 39.2 mg (0.0358 mmol, 68%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.49 (s, 1 H, CH=N), 9.29 (s, 1 H, CH=N), 9.14 (s, 1 H, CH=N), 9.04 (s, 1 H, CH=N), 8.88 (d, ^4J = 3.1 Hz, 1 H, ArH), 8.73 (d, ^4J = 3.1 Hz, 1 H, ArH), 8.37 (s, 1 H, ArH), 8.34 (s, 1 H, ArH), 8.00–8.11 (m, 3 H, ArH), 7.90 (d, ^3J = 8.8 Hz, 1 H, ArH), 7.62 (d, ^4J = 2.6 Hz, 1 H, ArH), 7.34 (t, ^3J = 7.8 Hz, 2 H, ArH), 7.26 (t, ^3J = 7.6 Hz, 2 H, ArH), 7.23 (d, ^4J = 2.7 Hz, 1 H, ArH), 6.49 (dt, ^3J = 7.7, ^4J = 2.7 Hz, 2 H, ArH), 1.49 [br., 18 H, two C(CH$_3$)$_3$ groups overlap], 1.46 [s, 9 H, C(CH$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, [D$_6$]DMSO): δ = 172.23, 172.16, 170.81, 166.95, 163.79, 162.69, 162.33, 162.14, 144.67, 142.46, 141.64, 141.54, 139.85, 139.47, 139.15, 138.67, 138.03, 137.54, 135.79, 135.46, 134.77, 134.60, 132.61, 131.67, 130.98, 130.64, 127.56, 125.74, 123.96, 122.53, 120.97, 119.52, 119.46, 117.36, 116.72, 115.40, 114.35, 112.75, 112.48, 102.53, 35.34, 35.07, 34.92, 29.53 [2 × C(CH$_3$)$_3$], 29.20 ppm. MS (MALDI+, pyrene): *m*/*z* = 1094.2 [M + H]$^+$. $C_{52}H_{47}BrN_6O_8Zn_2{\cdot}0.5H_2O$ (1103.74): calcd. C 56.59, H 4.38, N 7.61; found C 56.45, H 4.37, N 7.61.

Bis-Ni(salphen) Complex 13: To a solution of mono-Zn complex **2** (120.4 mg, 0.152 mmol) in THF (100 mL) was added a solution of 3-*tert*-butylsalicylaldehyde (49.3 mg, 0.277 mmol) in MeOH (10 mL) and subsequently a solution of $Ni(OAc)_2{\cdot}4H_2O$ (111.7 mg, 0.449 mmol) in MeOH (10 mL). The dark red-brown solution was stirred for 18 h, filtered, and the filtrate was concentrated. Trituration with MeOH (40 mL) furnished a brown solid after filtration and drying. Yield: 103.9 mg (0.104 mmol, 68%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.04 (s, 1 H, CH=N), 8.80 (s, 1 H, CH=N), 8.77 (s, 1 H, CH=N), 8.60 (s, 1 H, CH=N), 8.40 (m, 1 H, ArH), 8.28 (s, 1 H, ArH), 8.13 (m, 1 H, ArH), 7.97–8.03 (m, 2 H, ArH), 7.69–7.71 (m, 2 H, ArH), 7.46–7.51 (m, 2 H, ArH), 7.22–7.30 (m, 3 H, ArH), 6.59–6.67 (m, 3 H, ArH), 1.40 [br. s, 27 H, 3 × C(CH$_3$)$_3$] ppm. The compound is too insoluble for a decent ^{13}C-NMR spectroscopic analysis. MS (MALDI+, pyrene): *m*/*z* = 1000.2 [M$^+$], 2004.4 [2M + H]$^+$. $C_{52}H_{48}N_6Ni_2O_8$ (1002.36): calcd. C 62.31, H 4.83, N 8.38; found C 62.07, H 4.96, N 8.43.

Crystal Data for 12: $C_{56}H_{58}N_6O_{11.5}Zn_2$, M_r = 1129.82, triclinic, $P\bar{1}$, a = 13.6205(8) Å, b = 14.3234(8) Å, c = 15.1813(11) Å, α = 78.444(2)°, β = 64.902(2)°, γ = 80.902(2)°, V = 2618.8(3) Å^3, Z = 2, ρ = 1.433 g cm^{-3}, μ = 0.985 mm^{-1}, λ = 0.71073 Å, T = 100(2) K, F(000) = 1176, θ(min) = 1.46°, θ (max) = 33.20°, 18360 reflections collected, 11975 reflections unique (R_{int} = 0.0312), GOF = 1.049, R_1 = 0.0608 and wR_2 = 0.1764 [$I > 2\sigma(I)$].

CCDC-724935 contains 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): Experimental procedures and analytical data for all new compounds, full structural details for **12** and NMR spectroscopic details for the conversion of **11** into **15**.

Acknowledgments

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[1] a) J. F. Larrow, E. N. Jacobsen, *Top. Organomet. Chem.* **2004**, *6*, 123; b) L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85; c) T. Katsuki, *Chem. Soc. Rev.* **2004**, *33*, 437; d) P. G. Cozzi, *Chem. Soc. Rev.* **2004**, *33*, 410.
[2] S. J. Wezenberg, A. W. Kleij, *Angew. Chem. Int. Ed.* **2008**, *47*, 2354.
[3] A. W. Kleij, *Chem. Eur. J.* **2008**, *14*, 10520.
[4] A. W. Kleij, *Eur. J. Inorg. Chem.* **2009**, 193.
[5] P.-H. Aubert, P. Audebert, M. Roche, P. Capdevielle, M. Maumy, G. Ricart, *Chem. Mater.* **2001**, *13*, 2223.
[6] For a supramolecular approach toward heteromultimetallic systems see: S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2008**, *47*, 2925.

[7] S. Curreli, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *J. Org. Chem.* **2007**, *72*, 7018.

[8] S. Curreli, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Eur. J. Inorg. Chem.* **2008**, 2863.

[9] In some cases, we observed imine equilibration of mono-Zn complex **2** after prolonged standing in [D_6]DMSO.

[10] Transmetalation of Zn(salphen) complexes has been previously reported: a) E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2007**, *46*, 7265; b) S. J. Wezenberg, G. A. Metselaar, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chim. Acta* **2009**, *362*, 1053.

[11] a) A. R. van Doorn, D. J. Rushton, M. Bos, W. Verboom, D. N. Reinhoudt, *Recl. Trav. Chim. Pay-Bas.* **1992**, *111*, 415; b) L. Jin, Y. Huang, H. Jing, T. Chang, P. Yan, *Tetrahedron: Asymmetry* **2008**, *19*, 1947.

[12] A. L. Singer, D. A. Atwood, *Inorg. Chim. Acta* **1998**, *277*, 157.

[13] 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.

[14] a) C. T. L. Ma, M. J. MacLachlan, *Angew. Chem. Int. Ed.* **2005**, *44*, 4178; b) J. K.-H. Hui, Z. Yu, M. J. MacLachlan, *Angew. Chem. Int. Ed.* **2007**, *46*, 7980.

[15] S. J. Wezenberg, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2008**, *10*, 3311.

[16] E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans.* **2008**, 734.

[17] Although structure **11** can be easily demetalated in the presence of imidazole under these conditions, the use of the nonsymmetric bis-Zn(salphen) complexes in catalysis is not hampered, since sufficient stabilization of the metal ions can be obtained through coordination of solvent molecules and/or substrates and introduction of appropriate substituents on the phenyl side groups of the Zn(salphen) units.

[18] We have focused on the use of complex **11** for selective demetalation of the monomeric site; the other bis-Zn(salphen) complexes (except for **6**) have insufficiently large substituents on each 3- or 3′-position of the bis-salen ligand, and therefore the difference in stability between the two Zn(salphen) units is considered too minimal for a selective conversion.

[19] Mono-Zn(salphen) complex **2** was also used as a starting point for direct heterobimetallic complex formation by using $Ni(OAc)_2{\cdot}4H_2O$ and various salicylaldehydes in $CHCl_3$/MeOH as medium. In all cases, both ^{1}H NMR spectroscopy as well as MALDI-TOF-MS clearly indicated the isolation of a mixture of compounds due to transmetalation of the Zn(salphen) module (see ref.[10]). As a result, both homo- and heterobimetallic species were observed.

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