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Expedient Method for the Transmetalation of Zn(II)-Centered Salphen Complexes

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Various mono- and bis-Zn^{II} complexes derived from salphen ligands have been conveniently transmetalated with a number of transition metal (TM) acetates (M = Ni, Pd, Mn) in THF to afford their respective TM–salphen counterparts in excellent isolated yields (80–100%). This new transmetalation procedure allows in situ switching between supramolecular and catalytic functions of the metallosalphen complex.

Catalysis is at the forefront of science, playing an important role in the development of more sustainable chemical and pharmaceutical processes. In the field of homogeneous catalysis, salen ligands[1] have been investigated for many years. Currently these compounds are among the most widely developed ligands in the catalysis toolbox of modern chemistry for a range of organic transformations. Many synthetic approaches toward metallosalen complexes are known that start off with double Schiff base precursors. These precursors commonly originate from a condensation process involving 1 equiv of a diamine and 2 equiv of salicylaldehyde or ketone analogue. Their respective metal salts are generally easily obtained by treatment with acetate-based metal precursors or via activation of the two phenolic positions with a strong base (e.g., BuLi or $ZnEt_2$).[2] The resultant metallosalen frameworks are thermally and kinetically stable entities controlled by the presence of a tetradentate ligation mode of the N_2O_2 pocket that is characteristic of the salen ligand. This stabilization ability allows, for instance, the creation of vital catalytic intermediates generated by a change in or accommodation of a higher oxidation state of the metal ion complexed by the salen ligand.[3]

Recently, we and others have been active in the development of new applications for salen frameworks with an emphasis on its supramolecular potential.[4] In particular, Zn^{II}-based salphen [salphen = *N*,*N*′-phenylenebis(salicylideneimine)] structures have been identified as excellent, nonreactive supramolecular components/templates. Their supramolecular potential has been recently used in the assembly of new homogeneous catalysts that showed unconventional selectivities and reactivities, as well as in noncovalently assembled boxlike structures.[5] The Lewis acidity of the Zn^{II} ion in these complexes allows easy formation of five-coordinate, (distorted) square pyramidal surrounded Zn^{II} in the presence of suitable donor systems including pyridines, furans, alcohols, nitriles, and water.[6] We envisioned that the high Lewis acid character of the Zn^{II} metal center in the

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(1) See for recent reviews on salen structures: (a) Leung, A. C. W.; MacLachlan, M. J. J. *Inorg. Organomet. Polym. Mater*. **2007**, *17*, 57. (b) Larrow, J. F.; Jacobsen, E. N. *Top. Organometal. Chem*. **2004**, *6*, 123. (c) McMarrigle, E. M.; Gilheany, D. G. *Chem. Rev*. **2005**, *105*, 1563. (d) Canali, L.; Sherrington, D. C. *Chem. Soc. Rev*. **1999**, *28*, 85. (e) Katsuka, T. *Adv. Synth. Catal*. **2002**, *344*, 131.

(2) For some representative routes toward (metallo)salens: (a) Morris, G. A.; Zhou, H.; Stern, C. L.; Nguyen, S. B. *Inorg. Chem*. **2001**, *40*, 3222. (b) Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem*. **1994**, *59*, 1939. (c) Holbach, M.; Zheng, X.; Burd, C.; Jones, C. W.; Weck, M. *J. Org. Chem*. **2006**, *71*, 2903.

(3) For some illustrative examples of such catalytic intermediates see: (a) Finney, N. S.; Pospisil, P. J.; Chang, S.; Palucki, M.; Konsler, R. G.; Hansen, K. B.; Jacobsen, E. N. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1720. (b) Belokon, Y. N.; North, M.; Maleev, V. I.; Voskoboev, N. V.; Moskalenko, M. A.; Peregudov, A. S.; Dmitriev, A.; Ikonnikov, N. S.; Kagan, H. B. *Angew. Chem., Int. Ed*. **2004**, *43*, 4085. (c) Feichtinger, D.; Plattner, D. A. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1718. (d) Zheng, X.; Jones, C. W.; Weck, M. *J. Am. Chem. Soc*. **2007**, *129*, 1105. (e) Man, W.-L.; Tang, T.-M.; Wong, T.-W.; Lau, T.-C.; Peng, S.-M.; Wong, W.-T. *J. Am. Chem. Soc*. **2004**, *126*, 478.

(4) (a) Sun, S.-S.; Stern, C. L.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc*. **2004**, *126*, 6314. (b) Splan, K. E.; Massari, A. M.; Morris, G. A.; Sun, S.-S.; Reina, E.; Nguyen, S. T.; Hupp, J. T. *Eur. J. Inorg. Chem*. **2003**, 2348. (c) Gianneschi, N. C.; Bertin, P. A.; Nguyen, S. T.; Mirkin, C. A.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc*. **2003**, *125*, 10508. (d) Gianneschi, N. C.; Cho, S.-H.; Nguyen, S. T.; Mirkin, C. A. *Angew. Chem., Int. Ed*. **2004**, *43*, 5503. (e) Kuil, M.; Goudriaan, P. E.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Commun*. **2006**, 4679. (f) Kuil, M.; Goudriaan, P. E.; Kleij, A. W.; Tooke, D. M.; Spek, A. L.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Dalton Trans*. **2007**, 2311. (g) Kleij, A. W.; Kuil, M.; Tooke, D. M.; Spek, A. L.; Reek, J. N. H. *Inorg. Chem*. **2007**, *46*, 5829.

(5) (a) Kleij, A. W.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Commun*. **2005**, 3661. (b) Kleij, A. W.; Kuil, M.; Tooke, D. M.; Lutz, M.; Spek, A. L.; Reek, J. N. H. *Chem. Eur. J*. **2005**, *11*, 4743. (c) Kleij, A. W.; Reek, J. N. H. *Chem. Eur. J*. **2006**, *12*, 4218.

(6) (a) Singer, A. L.; Atwood, D. A. *Inorg. Chim. Acta* **1998**, *277*, 157. (b) Kleij, A. W.; Kuil, M.; Lutz, M.; Tooke, D. M.; Spek, A. L.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Inorg. Chim. Acta* **2006**, *359*, 1807.

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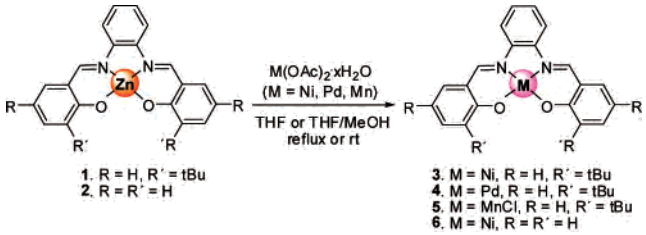
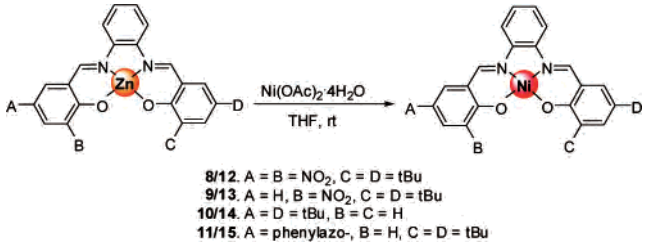
Scheme 1. Synthesis of Compounds **3**−**6** via Transmetalation



Scheme 2. Transmetalation of Zn^{II}−salphens **8**−**11**



salphen complexes may be used as a starting point for the preparation of TM-derived complexes through a transmetalation procedure[7] to furnish thermodynamically more stable structures. If successful, this could open pathways to multipurpose systems of which the (catalytic) properties may be controlled via in situ exchange of the metal ion, or simply lead to the selective exchange of Zn centers for other TM ions in multimetallic salphen derivatives,[8] thereby potentially giving access to interesting heterometallic structures. Herein we communicate a versatile synthetic approach aimed at metal exchange within Zn^{II}−salphen structures and the main factors governing the rate of metal exchange in the salphen framework. To our knowledge, this is the first example of a transmetalation process within a tetradentate salen framework with an ample scope.

Our first attempt at metal exchange was carried out with Zn^{II}-salphen complex **1** and 1 equiv of $Ni(OAc)_2 \cdot 4H_2O$ at RT using THF as the solvent. Although THF will occupy the fifth, apical coordination site and therefore may stabilize the Zn^{II}−salphen in solution,[6a] a gradual change in color from yellow to red of the reaction mixture was noted in time which was attributed to Ni^{II}−salphen formation. The drastic color change and ^1H NMR spectroscopy proved to be both very helpful tools to determine the time-dependency of the desired conversion. Under the applied conditions, a conversion of 12% was observed after 15 min, and complex **3** was isolated in 95% yield after 16 h and appropriate workup. Since the metal center in the Ni^{II}−salphen complex is much less Lewis acidic, diagnostic shifts are generally observed for the imine

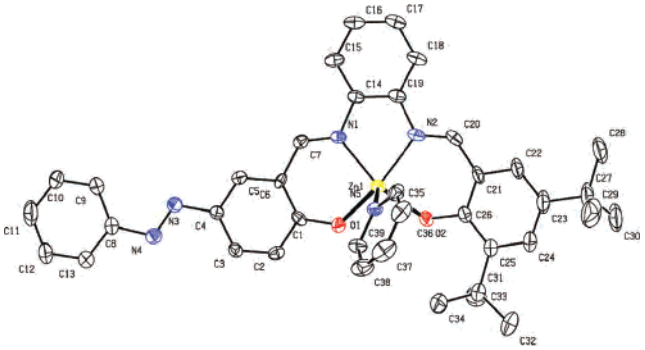


Figure 1. X-ray molecular structure for **11** with the adopted numbering scheme. Co-crystallized solvent molecules and H atoms are deleted for clarity.

protons as compared to the Zn(salphens) (see Supporting Information). For **3**, the imine groups resonate at 8.74 ppm (acetone-d_6) while the parent Zn^{II} complex showed a single imine peak much more downfield (9.05 ppm). We then extended the approach toward other TMs, and complexes **4** (M = Pd^{II}, 82%) and **5** (M = $Mn^{III}Cl$, 89%) were obtained in high yield using similar preparations. The simple isolation of complex **5** illustrates the usefulness of the transmetalation procedure, since Mn^{III}-centered salens have a long-standing tradition in homogeneous catalysis.[2b]

Interestingly, in the case of **4**, the initial transmetalation protocol was carried out at RT and proved to be much slower as compared to **3** and **5**, and only a conversion of 8% was obtained after 3 h. This points at some steric effect of the 3-positioned *t*-Bu groups in the salphen ligand upon metal exchange with larger metals ions. This was further corroborated by the synthesis of **6** (92%) which proceeded via Zn(salphen) **2** (note the absence of 3-*t*-Bu groups), and an almost *immediate* color change from yellow to deep red was noted, in contrast to the synthesis of **3**.[9]

Next, the transmetalation procedure was examined for a range of different (non-)symmetric Zn(salphens) with either electron-donating or -withdrawing groups located at the phenyl side-groups to further investigate the scope of the discovered transmetalation procedure. Zn(salphen) complexes **8**−**11** were prepared in good yields (62−88%) using the previously reported monoimine **7** (Supporting Information)[10] and a recently published one-pot, two-step procedure.[11] All new compounds were fully characterized (see Supporting Information) and for the pyridine adduct of **11**, the X-ray crystal structure was also determined as a representative model for nonsymmetric Zn(salphen) complexes (Figure 1).

Complex **11** was crystallized from bulk CH_3CN containing about 5% pyridine (v/v). As expected, the structure for **11** shows a pentacoordinated Zn center with the axial coordination site occupied by a pyridine ligand. Furthermore, the

(7) For a transmetalation process carried out with oxime-based salen derivatives: Akine, S.; Taniguchi, T.; Nabeshima, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 4670. However, in these structures only the central all-oxygen-coordinated lanthanide metal ion is replaced whereas the 'salen'-ligated metal centers (M = Zn) remain unaffected.

(8) For a few recent examples of multimetallic salen-type systems see: (a) Gallant, A. J.; Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 5248. (b) Hui, J. K.-H.; MacLachlan, M. J. *Chem. Commun.* **2006**, 2480. (c) Ma, C. T. L.; MacLachlan, M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 4178. (d) Gallant, A. J.; MacLachlan, M. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 5307. (e) Akine, S.; Taniguchi, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2006**, *128*, 15765. (f) Akine, S.; Sunaga, S.; Taniguchi, T.; Miyazaki, H.; Nabeshima, T. *Inorg. Chem.* **2007**, *46*, 2959.

(9) We also tested the transmetalation of related Zn(salphen) complex **10** with $Pd(OAc)_2$ under similar conditions and compared the conversion data with those obtained in the syntheses for **4** and **14**. The results (see Supporting Information) revealed both an electronic and a steric influence in the transmetalation protocol.

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

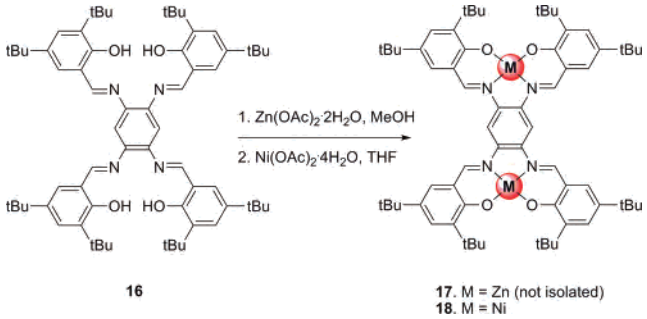
(11) Kleij, A. W.; Tooke, D. M.; Spek, A. L.; Reek, J. N. H. *Eur. J. Inorg. Chem.* **2005**, 4626.

central N_2O_2 pocket of the salphen ligand seems readily accessible for suitable electrophiles (cf. metal reagent) since one of the two phenyl side-groups is not substituted at the 3-position. Interestingly, the crystal enclosed two distinct conformations for **11** for which a number of bond distances and angles around the central N_2O_2 pocket were clearly different.[12,13] The axial pyridine ligand in both conformations showed no disorder but is nonsymmetrically situated above the plane defined by the N and O atoms of the salphen ligand.[11]

The transmetalation procedures that involved **8**−**11** affording Ni(salphens) **12**−**15** were simply visually followed, and full conversions were supported in all cases by separate ^{1}H NMR analyses. It should be noted that the color change (from yellow-orange to deep red) in the case of **12**−**13** was significantly faster than observed for both **14** and **15**, which points at an electronic influence of the pendant groups on the salphen framework. Complexes **12**−**15** were isolated in excellent yield (90−100%) and fully analyzed by NMR, MS, and elemental analyses (Supporting Information). In particular, Ni(salphen) derivatives **12** and **13** proved to be sparingly soluble in the common organic solvents, which is ascribed to the presence of nitro-aryl groups; this causes a fast crystallization, even from DMSO.

Additionally, the transmetalation of the known bis-Zn^{II} complex of tetraimine **16**[14] was considered as a probe for the introduction of multiple TM metal centers in multimetallic Zn(salphen) species. The subject of multimetallic salen synthons is currently attracting profound interest in the field of functional materials.[8] The bis-Zn^{II}−salphen complex

Scheme 3. In Situ Transmetalation of bis-salphen−Zn_2 Complex **17**



16

17. M = Zn (not isolated)
18. M = Ni

17[5b] was generated in situ and directly submitted to the transmetalation protocol by changing the solvent from MeOH to THF, but essentially without isolation of intermediate **17**. After the addition of the Ni^{II} reagent, the evident change in color from orange to deep purple-red unambiguously revealed the formation of bis-Ni^{II}−salphen **18**, and this compound was isolated in 88% yield. MS analysis provided unambiguous evidence for the formation of **18** since the presence of two Ni centers is easily recognized in the observed isotope pattern.

In conclusion, we here present a facile and effective method for the transmetalation of readily available symmetrical and nonsymmetrical Zn^{II}−salphen complexes. Zn^{II}−salphen derivatives have recently proven to be excellent supramolecular building blocks.[4g,5,6b] An appropriate transmetalation (e.g, a Zn^{II}-for-Mn^{III} exchange, cf. compound **5**) will allow a predetermined change in the properties of the metallosalphen unit. This approach will be beneficiary in cases where it is desired to change the catalytic/supramolecular properties of the salphen complex in situ (cf., complex **18**). Besides, selective exchange of one of the Zn^{II} ions in **17** affords interesting heterobimetallic metallosalphens that will have significance as multifunctional materials and/or catalysts. Multistage, one-pot catalytic conversions based on this expanded salen technology may now be designed to produce more efficient chemical processes. Studies directed toward this challenging goal are presently ongoing in our laboratory.

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Supporting Information Available: Crystallographic details for the structure of compound **11** (in CIF format), detailed experimental and analytical details for all new derivatives, and known compounds **5**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) Some crystallographic details for **11**: $C_{39}H_{39}N_5O_2Zn$, M_w = 675.12, triclinic $P\bar{1}$, a = 7.3337(2) Å, b = 10.8421(2) Å, c = 22.8755(7) Å, α = 100.664(2)°, β = 96.051(2)°, γ = 104.0700(10)°, Z = 2, ρ = 1.310 Mg/M^3, reflections collected 33 881, independent 11 004, GOF on F^2 = 0.968, R1 = 0.0482, wR2 = 0.1267.

(13) For **11** two different disordered orientations in the crystal were found in a 56:44 ratio, which is the consequence of two distinct conformational positions of the phenylazo unit. Only the Zn(1), O(1), O(2), and pyridine atoms are located on unique positions in the crystal lattice. Some small deviations are found as compared to a similar nonsymmetric Zn(salphen) analogue (see ref 10). Selected bond distances-(Å)/angles(deg) for **12** with esd's: Zn(1)−O(1) = 1.9760(11), Zn(1)−O(2) = 1.9972(11), Zn(1)−N(2′) = 2.016(16), Zn(1)−N(1) = 2.073(11), Zn(1)−N(5) = 2.1038(17), Zn(1)−N(2) = 2.109(11), Zn(1)−N(1′) = 2.194(13), O(1)−Zn(1)−(O2) = 96.96(4), O(1)−Zn(1)−N(2′) = 153.8(5), O(2)−Zn(1)−N(2′) = 92.9(4), O(1)−Zn(1)−N(1) = 91.94(17), O(2)−Zn(1)−N(1) = 156.3(2), N(2′)−Zn(1)−N(1) = 70.6(4), O(1)−Zn(1)−N(5) = 95.62(6), O(2)−Zn(1)−N(5) = 93.80(6), N(2′)−Zn(1)−N(5) = 107.9(5), N(1)−Zn(1)−N(5) = 107.2(3), O(1)−Zn(1)−N(2) = 160.3(4), O(2)−Zn(1)−N(2) = 86.2-(3), N(2′)−Zn(1)−N(2) = 8.2(6), N(1)−Zn(1)−N(2) = 78.4(3), N(5)−Zn(1)−N(2) = 103.5(4), O(1)−Zn(1)−N(1′) = 83.8(2), O(2)−Zn(1)−N(1′) = 160.4(4), N(2′)−Zn(1)−N(1′) = 79.1(4), N(1)−Zn(1)−N(1′) = 8.5(3), N(5)−Zn(1)−N(1′) = 105.6(4), N(2)−Zn(1)−N(1′) = 86.9(3).

(14) Chichak, K.; Jacquemard, U.; Branda, N. R. *Eur. J. Inorg. Chem.* **2002**, 357.