DOI: 10.1002/ejoc.201100745

Synthesis of Tetrahedral Shape-Persistent Tetranuclear Metal–salphens

Michael Mastalerz*[a] and Iris M. Oppel[b]

Keywords: Synthesis design / Zinc / Nickel / Palladium / UV/Vis spectroscopy / N,O ligands

The synthesis of two novel tetrakis(salicylaldehydes) based on a rigid tetraphenylmethane core is presented. These salicylaldehydes were used as precursors for the construction of three-dimensional multimetallic salphens, as exemplified by the synthesis of rigid and shape-persistent tetranuclear zinc–, nickel– and palladium–salphens with defined geometries and distances between the metal sites. The UV/Vis measurements of the tetranuclear metal complexes are presented.

Introduction

The Schiff base condensation reaction[1] is a versatile and powerful synthetic tool due to the fact that the formation of imines is a reversible process. Furthermore, the reversibility of the reaction allows the system to eventually reach the thermodynamically most stable product. Therefore, the Schiff base condensation reaction is one of the most investigated reactions used in dynamic covalent chemistry or systems chemistry.[2] It is widely exploited to synthesize shape-persistent macrocycles,[3] cage compounds,[4] or helicates[5] from relatively simple molecules in a single step and usually in high yields. Even sophisticated molecules such as borromean rings are readily accessible in high yields in one step through a combination of imine bond formation and metal complexation.[6]

Of the numerous Schiff bases, tetradentate salens or salphens, derived from salicylaldehydes and diamines, are known for their extraordinary ability to complex a large variety of metal ions. These metal complexes are excellent catalysts for a wide range of transformations, in particular, for enantioselective reactions[7] or for the fixation of CO_2 as cyclic carbonates or polymeric lactones.[8,9] In addition to their application as homogeneous catalysts, metal–salphens also serve as a construction motif for the formation of supramolecular assemblies or novel functional materials.[10] It is known that the cooperative effects of two or more metal–salphen sites play an important role in several catalytic reactions.[11] Therefore, efforts have been made to synthesize molecular structures with multiple salphen/salen binding pockets, offering the possibility of placing two or more (catalytically active) metal centers in a predefined three-dimensional geometry.[12] The majority of investigated oligometallic salphen systems contain two metal centers, either with the same metal species (homodimetallic)[12,13] or, rarely, with two different metals (heterodimetallic).[14] Most of the previously mentioned macrocyclic[3] systems contain three salphen pockets. In addition, Glaser and co-workers introduced planar compounds with three metal–salphen units, the magnetic properties of which were investigated as well as the cooperative effects in catalytic reactions.[15] MacLachlan and co-workers described the first three-dimensional trinuclear nickel–salphens based on triptycenes, having high surface areas in the solid state.[16] With the exception of polymeric systems,[17] discrete compounds containing more than three salphen pockets, which are covalently connected to each other, are to the best of our knowledge very rare, and only two examples have recently been described in the literature.[18] One example is that of MacLachlan and co-workers,[18a] who synthesized two different kinds of salphen pockets in a stepwise manner, first by the (irreversible) formation of ketimine bonds and secondly by the reversible formation of aldimine bonds. However, no metal ion incorporation into the salphen pockets has been described to date. Very recently, Kleij and co-workers described the cooperative self-assembly of tetranuclear salphen macrocycles containing either four zinc or four palladium centers.[18b] In almost all of the compounds mentioned above, the salphen pockets are arranged in a planar 2D structure. Therefore, we envisaged the synthesis of tetrahedral tetrakis(salicylaldehydes) that will serve as precursors for the synthesis of 3D multinuclear salphen compounds, dendrimers, or even extended polymeric structures with different properties in comparison with the "flat" systems. For this purpose we chose the well-known tetraphenylmethane[19] as a core unit, which has previously been demonstrated to serve as an ideal subunit in the construction of rigid tetraaromatic compounds, which are ideal for studying homoconjugation or energy-transfer mecha-

[a] Organic Chemistry II & Advanced Materials, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany
Fax: +49-731-50-22840
E-mail: michael.mastalerz@uni-ulm.de
[b] Institute of Inorganic Chemistry, RWTH Aachen, Landoltweg 1, 52074 Aachen, Germany
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201100745.

nisms.[20] Furthermore, this core unit has been exploited as a molecular precursor for the synthesis of discrete polyphenylene dendrimers.[21]

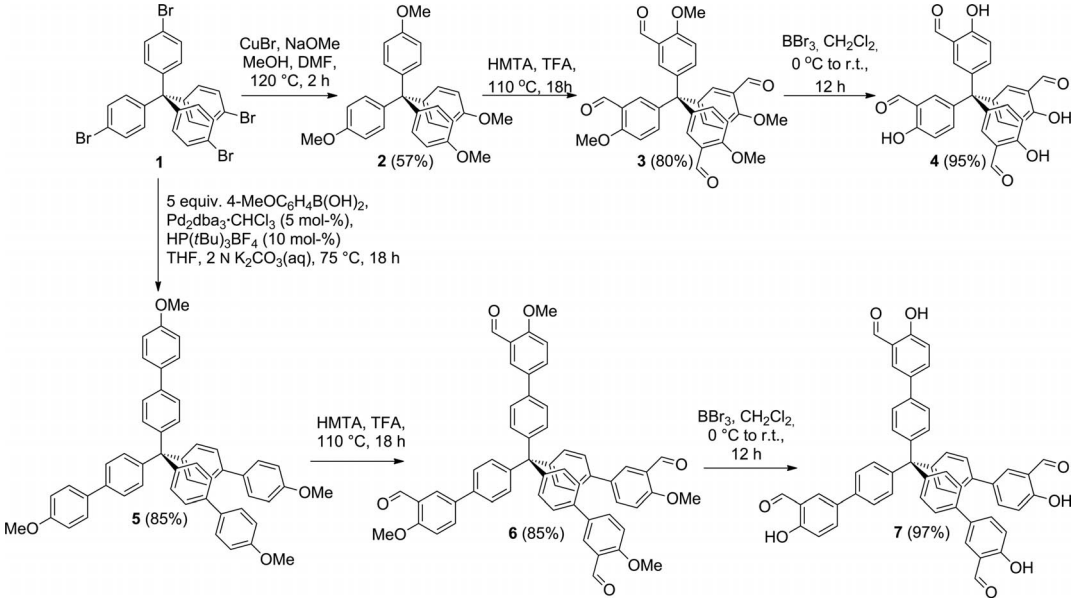
Herein we present the synthesis of the first tetrahedral tetrakis(salicylaldehydes) **4** and **7**, which have been used for the construction of three-dimensional tetranuclear metal–salphens. In addition, the photophysical properties of the various tetranuclear metal–salphens are discussed.

Results and Discussion

Synthesis and Characterization

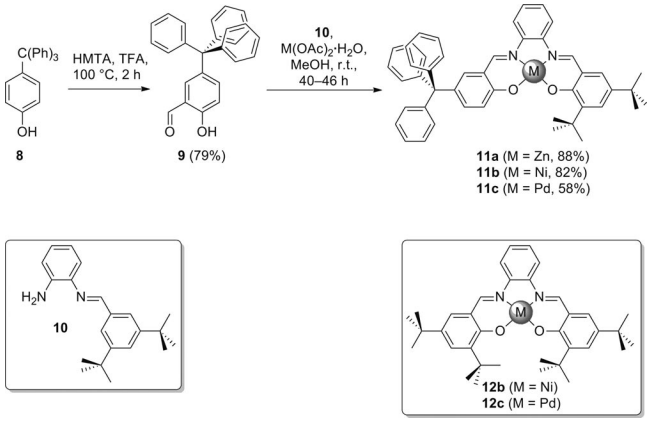
The tetrakis(salicylaldehydes) **4** and **7** were synthesized by starting with tetrakis(*p*-bromophenyl)methane (**1**), which is easily accessible by bromination of tetraphenylmethane.[22] To obtain the smaller salicylaldehyde **4**, **1** was first converted into the tetramethoxylated compound **2** in 57% yield by a copper-mediated cross-coupling reaction with sodium methoxide in a solvent mixture of dimethylformamide (DMF) and methanol (Scheme 1).[23] The next step was the Duff formylation of **2** with hexamethylenetetraamine (HMTA) in anhydrous trifluoroacetic acid, which gave tetraaldehyde **3** in 80% yield.[24] Subsequent demethylation with BBr_3 in dry dichloromethane provided the tetrakis(salicylaldehyde) **4** almost quantitatively.[25] This reaction sequence (first the Duff formylation, then the deprotection) is preferred, because it is known that *para*-substituted methoxylated arenes give the mono-*ortho*-formylated products exclusively, whereas the more reactive phenols can further react to the *ortho*-diformylated salicyldialdehydes, leading to a complex mixture of products, which is difficult to separate.[24] The homologue tetrakis(salicylaldehyde) **7** with additional 1,4-phenylene units was synthesized by a four-fold Suzuki–Miyaura reaction of tetrabromide **1** with *p*-methoxyphenylboronic acid, which gave 85% yield of the corresponding tetrakis(biphenylyl)methane **5**.[26] Formylation and subsequent BBr_3-promoted cleavage of the methyl groups finally gave the tetrakis(salicylaldehyde) **7** in high yield (83% over two steps).

Before using the tetraaldehydes **4** and **7** in Schiff base condensation reactions with **10**,[27] monoaldehyde **9** was synthesized from tritylphenol (**8**) as a model compound to optimize the reaction conditions for the preparation of unsymmetrical salphen–metal complexes **11a**–**c**, which can be viewed structurally as components of the final products **13a**–**c**, respectively (Scheme 2). Therefore, half-imine **10** was treated with aldehyde **9** and metal acetate in methanol at room temperature[28,29] to yield zinc–salphen **11a** as a bright-yellow solid, nickel–salphen **11b** as a brownish-red solid, and palladium–salphen **11c** as an orange solid in 88, 82, and 58% yields, respectively. In contrast to a literature procedure,[29] in which the salicylaldehyde was used in excess to obtain a higher conversion of the unsymmetrical zinc–salphen, we had to use half-imine **10** in excess: **10** is very soluble in the reaction solvent, whereas salicylaldehyde **9** is not. Therefore, the excess of **10** can easily be removed by washing the crude product several times with methanol. The conversion to unsymmetrical zinc–salphen **11a** is very clean, the ^{1}H NMR spectrum of the crude product showing exclusively the signals of the desired product. Instead, in the reaction of **9** and **10** in the presence of nickel(II) or palladium(II) acetate, the ^{1}H NMR spectra of the crude products revealed the formation of substantial amounts of the symmetrical metal–salphens **12b** and **12c**, which could be removed by crystallization from CH_2Cl_2/MeOH, leading to a lower yield (58%) of the unsymmetrical palladium–salphen **11c**. Zinc–salphen **11a** forms stable dimers $(\mathbf{11a})_2$ in the gas phase, which were detected by MALDI-TOF mass spectrometry; in the mass spectrum a peak at m/z = 1465



Scheme 1. Synthesis of tetrakis(salicylaldehydes) **4** and **7** starting from tetrakis(4-bromophenyl)methane (**1**).

can be observed in addition to the peak at m/z = 732 for the monomer **11a** (see the Supporting Information).[30] Such aggregate formation was not observed for the corresponding nickel– and palladium–salphens **11b** and **11c** under similar conditions.



Scheme 2. Synthesis of unsymmetrical metal–salphens **11a**–**c**.

By slow vapor diffusion of methanol into a solution of **11a** in DMF, we were able to grow single crystals suitable for X-ray diffraction (Figure 1):[30,31] **11a** crystallizes as dimers in the triclinic space group $P\bar{1}$. The analysis shows that the salphen backbones are bent out of plane. The Zn–N distances are 2.105(2) and 2.066(2) Å, and the distances for the intramolecular Zn–O bonds are 2.051(1) and 1.954(1) Å. The formation of dimers is favored by a second type of intermolecular Zn–O bond [d = 2.053(1) Å]. The O2 and Zn1 atoms form a parallelogram with Zn–O–Zn angles of 96.2 and 83.5°. The similar lengths of the inter- and intramolecular Zn–O bonds suggest a relatively strong interaction in the dimer. The zinc dimers are themselves arranged in a linear fashion, mainly through intermolecular π–π interactions between the imine groups and the adjacent aromatic ring (d = 3.26 Å) and CH–π interactions of the hydrogen atoms located in the *meta*-positions with respect to the imine bonds and the aromatic planes of the trityl subunits of adjacent molecules (d = 2.86 Å). Furthermore, the linear arrangements are connected by intermolecular CH–π interactions between the *tert*-butyl hydrogen atoms and the aromatic rings of the trityl subunit [d(H–C) = 3.00 Å] and π–π interactions between the aromatic rings of trityl subunits (d = 3.31 Å).

We tested the conditions elaborated for the model compounds for the synthesis of tetranuclear metal–salphens using tetrakis(salicylaldehyde) **4**, half-imine **10**, and metal acetate as the reactants (see Scheme 3). Tetranuclear zinc–salphen **13a** can be synthesized in 73% yield from methanol under similar conditions as model compound **11a** (Figure 1). The structure of **13a** was confirmed by ^{1}H NMR, IR, HRMS, and UV/Vis spectroscopy (see the Supporting Information). Zinc complex **13a** is poorly soluble in most common organic solvents except for polar, coordinating solvents such as DMF and DMSO, which probably can be

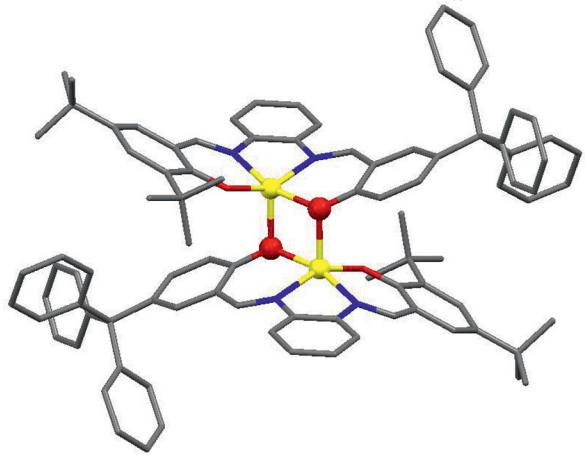
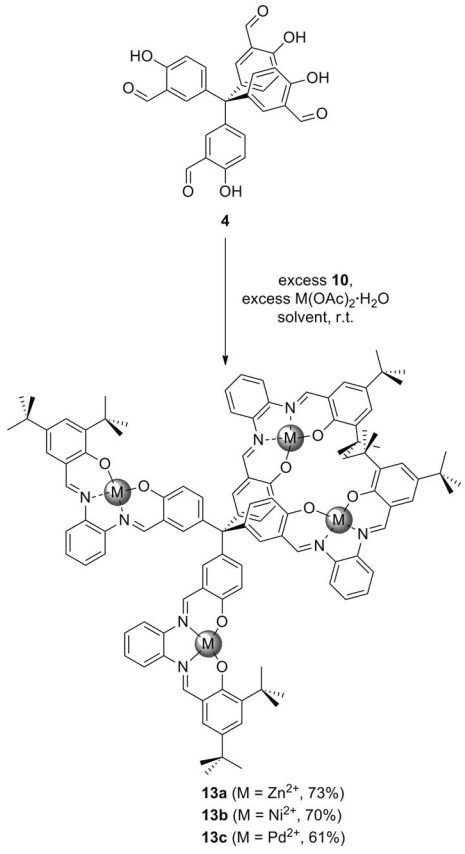


Figure 1. Crystal structure of **11a**. The dimer of the asymmetric unit is depicted along a nondefined crystallographic axis. Gray: carbon; blue: nitrogen; red: oxygen; yellow: zinc. The $(ZnO)_2$ cluster is depicted as a ball-and-stick-model. Hydrogen atoms have been omitted for clarity.

attributed to a relatively strongly bound network by formation of $(Zn–O)_2$ dimer subunits (see above). In the ^{1}H NMR spectrum, two peaks can be clearly assigned to the imine protons, the two singlets at δ = 8.92 and 8.73 ppm, which are comparable to the imine proton signals of the model compound **11a** (δ = 8.93 and 8.74 ppm). In the FTIR spectrum, the characteristic stretching band of the C=N bond appears at 1614 cm^{-1}, which again is comparable to that of the model compound **11a** (1614 cm^{-1}). In neither the ^{1}H NMR spectrum nor the IR spectrum can signals of residual formyl groups be detected, which suggests complete transformation of all four salicylaldehyde subunits of the precursor **4**. However, in the MALDI-TOF mass spectrum of **13a** a number of fragment peaks can be detected in addition to the molecular peak, which gives a hint of the instability of the tetranuclear zinc complex under the ionization conditions. This is in agreement with earlier findings by Kleij and co-workers, who demonstrated that zinc–salphens can be selectively decomposed in a directing fashion.[32]

In contrast to the synthesis of zinc complex **13a**, the reaction of **4** and **10** with nickel(II) acetate in methanol did not yield the tetranuclear nickel–salphen **13b** exclusively. Instead, incomplete reactions were observed, resulting in two- and three-fold reacted intermediates that are difficult to separate from the desired product **13b**. DMF was shown to be the solvent of choice. For a high conversion of **4** to tetranuclear **13b**, an excess (8 equiv.) of half-imine **10** was required to force the four-fold reaction to completion. Byproducts were removed by washing the crude product with DMF to give pure **13b** as a wine-red solid in 70% yield. As for the corresponding zinc complexes **13a** and **11a**, the similarity of the characteristic peaks of nickel complexes **13b** and **11b** in the ^{1}H NMR and IR spectra is clear: The protons of the imine bonds resonate at δ = 8.81 and 8.77 ppm for compound **13b** and are comparable to the signals at δ = 8.79 and 8.73 ppm for compound **11b**. The IR stretching of the imine bonds can be assigned to the strong

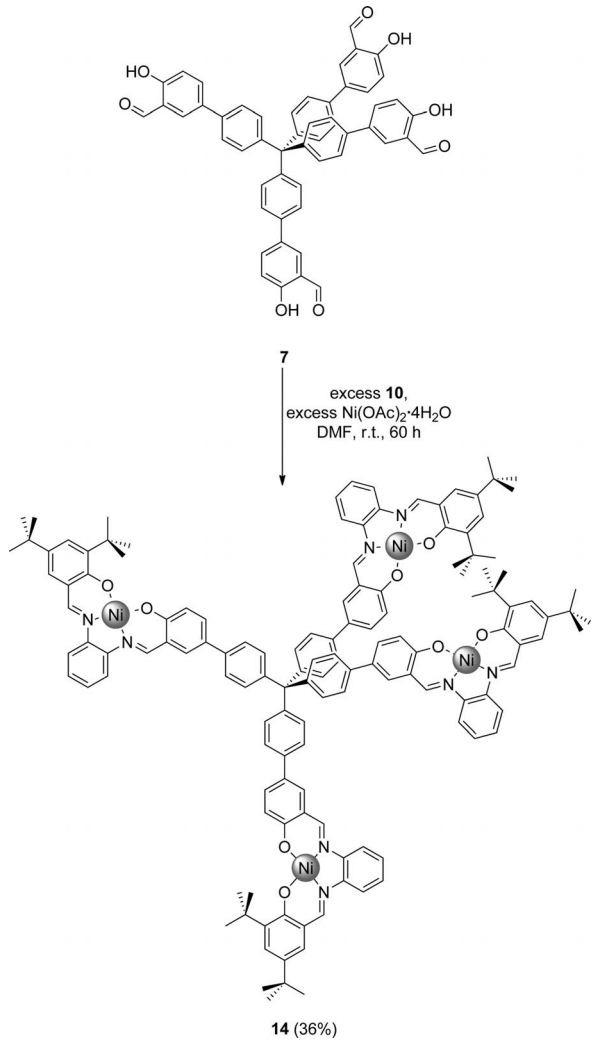


Scheme 3. Synthesis of tetrahedral tetranuclear metal–salphens **13a**–**c**. For the exact reaction conditions, see the Experimental Section.

bands at 1616 and 1614 cm^{-1} for **13b** and **11b**, respectively. The structure of **13b** was further confirmed by an intense base peak at *m*/*z* = 1950 in the MALDI-TOF mass spectrum. The isotopic pattern exactly fits the one calculated for the structure of **13b** (see the Supporting Information).

Tetranuclear palladium–salphen **13c** was synthesized by using DMF as solvent. Similarly to the model compound **11c**, the tetrakis(salphen) **13c** had to be isolated by several recrystallization steps (for details see the Experimental Section), giving the compound as a bright-orange solid in 61% yield. The ^{1}H NMR spectrum of **13c** shows characteristic peaks at δ = 9.15 and 9.06 ppm, which have been assigned to the protons of the imine bonds and, again, are comparable to the shifts of the imine protons of model compound **11c** in [D_6]DMSO (δ = 9.14 and 9.03 ppm). The MALDI-TOF mass spectrum shows a base peak at *m*/*z* = 2141 with an isotopic pattern as expected for $C_{113}H_{116}N_8O_8Pd_4$.

Because the tetranuclear nickel–salphen **13b** was less difficult to isolate, purify, and characterize than the corresponding zinc– and palladium–salphens **13a** and **13c**, we decided to test similar reaction conditions with elongated tetrakis(salicylaldehyde) **7** as reactant for the synthesis of the corresponding nickel–salphen congener **14** (Scheme 4), which we were able to isolate in 36% yield. The ^{1}H NMR and FTIR spectra (see the Supporting Information) show no peaks corresponding to aldehyde moieties, revealing full conversion of all four salicylic aldehyde units. In the ^{1}H NMR spectrum of **14**, the two characteristic singlets at δ = 8.82 and 8.98 ppm have been assigned to the imine protons. The MALDI-TOF mass spectrum shows a base peak at *m*/*z* = 2251, as expected.



Scheme 4. Synthesis of the larger tetranickel–salphen **14**.

In an initial experiment we tested whether all four zinc cations in **13a** can be exchanged by nickel ions and therefore can be a potential precursor for the templated synthesis of other tetranuclear tetrahedral metal–salphens that are difficult to access by the direct route depicted in Scheme 3.[33] Therefore, the tetranuclear zinc complex **13a** was dissolved in DMF, which resulted in a yellow solution, and an excess of nickel(II) acetate tetrahydrate was added. The reaction mixture immediately turned deep red, and a precipitate was formed. The wine-red precipitate was collected by filtration and washed with small portions of DMF. The ^{1}H NMR, MALDI-TOF mass, and FTIR spectra of this product are identical to those observed for **13b** synthesized according to Scheme 3, which demonstrates that the zinc complex **13a** serves as an efficient precursor for transmetalation reactions.

UV/Vis Spectroscopy

Depending on the nature of the metal, metal–salphen complexes are brightly colored (zinc: yellow; nickel: deep red; palladium: orange) and are used, for example, as optical sensors for the detection of explosives[34] or as the active material in organic light-emitting devices (OLEDs).[35] Therefore, we studied the metal–salphens by UV/Vis spectroscopic methods.

The UV/Vis absorption spectrum of tetranuclear zinc complex **13a** has a similar shape to that of the model compound **11a** and shows a maximum at λ_{max} = 415 nm with a shoulder at around 460 nm, which is comparable to results previously reported for similar zinc compounds (Figure 2).[34]

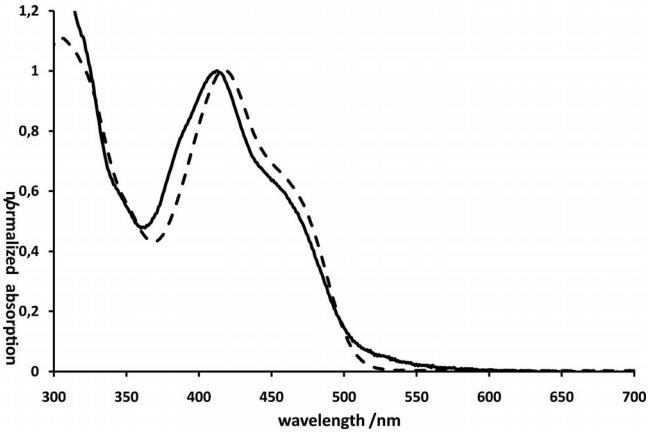


Figure 2. Comparison of the UV/Vis absorption spectra of the zinc–salphens **11a** (solid line) and **13a** (dashed line) in DMF as solvent ($c = 10^{-5}$ M). The spectra are normalized.

Similarly to the zinc complexes, the UV/Vis spectra of all three nickel–salphens have nearly the same adsorption bands (Figure 3). Complexes **11b** and **13b** each show a broad peak at λ_{max} = 496 nm with an onset at around 650 nm, which can be assigned to a CT from the metal to the ligand (MLCT band).[36] Furthermore, a relatively sharp maximum appears at λ_{max} = 387 and 389 nm, respectively, which derives from π–π* transitions in the ligands.[36]

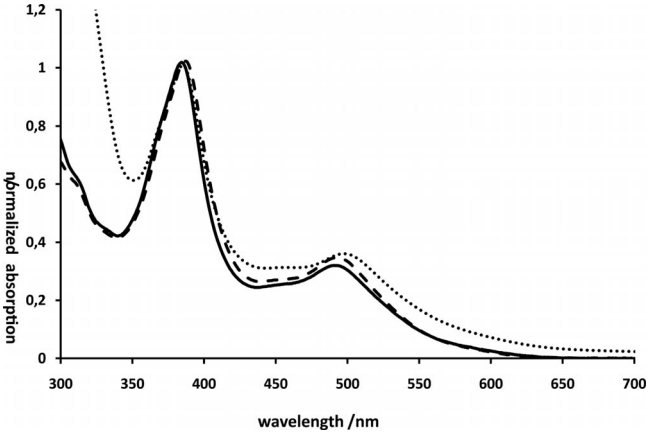


Figure 3. Comparison of the UV/Vis spectra of nickel–salphen complexes **11b** (solid line), **13b** (dashed line), and **14** (dotted line) in CH_2Cl_2 ($c = 10^{-5}$ M). The spectra are normalized for better comparison.

The palladium complexes **11c** and **13c** show broad MLCT bands at λ_{max} = 486 and 490 nm, respectively (Figure 4). Furthermore, in both spectra a shoulder appears at 387 and 383 nm, as well as three sharp overlapping peaks at λ_{max} = 363, 346, and 323 nm for **11c** and at λ_{max} = 363, 349, and 319 nm for **13c**.[37]

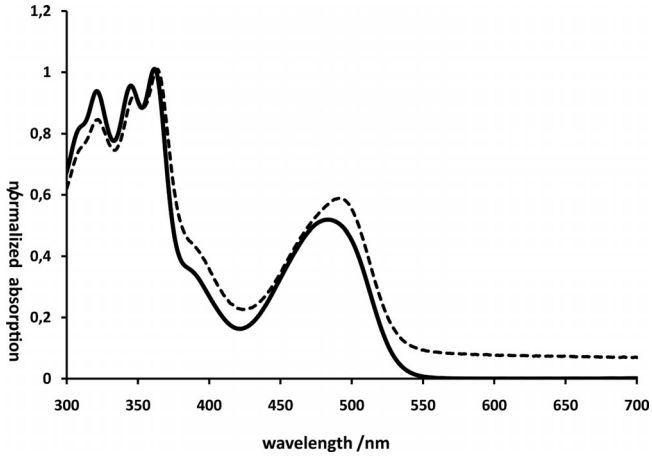


Figure 4. Comparison of the UV/Vis spectra of palladium–salphen complexes **11c** (solid line) and **13c** (dashed line) in DMF ($c = 10^{-5}$ M). The spectra are normalized for better comparison.

The adsorption maxima of the tetranuclear complexes **13a**–**c** are only slightly bathochromically shifted in comparison with the model compounds **11a**–**c**.

Conclusions

Two novel, rigid tetrahedral tetrakis(salicylaldehydes) have been synthesized. These salicylaldehydes are versatile building blocks for the synthesis of three-dimensional oligonuclear rigid metal–salphens with defined distances between the metal centers.[38] This was demonstrated by the full conversion of **4** and **7** into the corresponding tetranuclear zinc–salphen **13a**, the tetranuclear nickel–salphens **13b** and **14**, and palladium–salphen **13c**. These are, to the best of our knowledge, the first examples of discrete tetranuclear metal–salphen complexes with three-dimensional geometries. Currently, we are investigating the scope of the synthetic procedures to prepare tetranuclear metal–salphen complexes with various redox-active metal ions (e.g., Cu^{2+}, Co^{2+}, or Pt^{2+}) for detailed investigation of their electrochemical and optical properties to gain an insight into the intramolecular interactions of the distinct metal centers. In addition, we have employed **4** and **7** as rigid building blocks for the synthesis of novel extended three-dimensional polymeric metal–salphen/salen materials.[39] The results will be presented in due course.

Experimental Section

General: NMR spectra were recorded with a Bruker AMX 500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 125 MHz) or Avance 400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 100 MHz) spectrometer at 298 K, unless otherwise mentioned. Chemical shifts (δ) are given in ppm and were calibrated with residual non-deuteriated solvent peaks ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm; [D_8]THF: δ_H = 3.58 ppm, δ_C = 67.7 ppm; [D_6]DMSO: δ_H = 2.50 ppm) as internal standards. EI and CI mass spectrometry was performed with a Finnigan MAT SSQ-7000 or a Varian Saturn 2000 GC–MS instrument. MALDI-TOF mass spectra were recorded with a Bruker Daltonics Reflex III spectrometer by using dithranol or DCTB {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile} as matrix. UV/Vis absorption spectroscopy was performed with a Perkin–Elmer Lambda 19 spectrometer by using Merck Uvasol grade solvents. IR spectra were recorded as KBr pellets with a Perkin–Elmer FTIR Spectrum 2000 spectrometer. Melting points were measured with a Büchi B-545 apparatus. Elemental analyses were performed with an Elementar Vario EL instrument (Ulm University). Plastic sheets precoated with silica gel (Merck Si60 F_{254}) were used for thin-layer chromatography. Glass columns packed with Merck Silica 60 (mesh 40–60 μm) were used for flash-chromatographic purification. Solvents were purchased at ProLabo and distilled prior to use. If necessary, solvents were dried in advance by applying common procedures.[40] All reagents were purchased from commercial sources and used without further purification: Sodium methoxide (Merck, for synthesis), copper(I) bromide (Acros Organics, 98%), hexamethylenetetraamine (Fluka, 99%), trifluoroacetic acid (Solvay Fluorochemicals GmbH), boron tribromide (Merck, for synthesis), [Pd_2dba_3] (Alfa Aesar), HP(tBu)$_3$BF$_4$ (Aldrich, 97%), 4-methoxyphenylboronic acid (Alfa Aesar, 97%+), nickel(II) acetate tetrahydrate (Acros Organics, p.a.). Tetrabromide **1**[22] and half-imine **10**[27] were synthesized as described previously.

Synthetic Procedures

Tetrakis(4-methoxyphenyl)methane (2): In a screw-capped vial tetrabromide **1** (1.92 g, 3 mmol) and sodium methoxide (6.92 g, 128 mmol) were suspended in a mixture of anhydrous methanol (8.5 mL) and anhydrous DMF (20 mL). The mixture was heated to 110 °C (complete dissolution occurs), and CuBr (1.98 g, 13.7 mmol) was added in one portion. The reaction mixture turned bluish-gray. After 2–2.5 h, the reaction mixture was allowed to cool to room temperature, and 2 N hydrochloric acid (150 mL) and dichloromethane (150 mL) were added. The aqueous layer was extracted with dichloromethane (2 × 100 mL), and the combined organic extracts were washed with 2 N hydrochloric acid (2 × 100 mL), water (3 × 100 mL), and brine (200 mL), and the mixture was dried with sodium sulfate. After removing the solvents by rotary evaporation, the remaining residue was treated with methanol (10 mL), sonicated, and the off-white precipitate collected with a Büchner funnel. Washing with methanol (3 × 10 mL) and drying in vacuo gave 1.04 g of an off-white solid. Column chromatography (SiO_2, light petroleum ether/dichloromethane, 1:1) gave, after drying in vacuo, 760 mg (57%) of compound **2** as a colorless powder. M.p. 246–248 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (d, J = 8.8 Hz, 8 H, ArH), 6.77 (d, J = 8.8 Hz, 8 H, ArH), 3.79 (s, 12 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.39 (s, Ar*C*-OMe), 139.75, 132.00, 112.58, 62.21 (s, Ar_4C), 55.19 (q, O*C*H$_3$) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3020 (w), 2949 (w), 2930 (w), 2904 (w), 2835 (w), 1605 (m), 1575 (s), 1507 (s), 1466 (m), 1457 (m), 1442 (m), 1294 (m), 1250 (s), 1180 (s), 1117 (m), 1032 (s), 1011 (w), 942 (vw), 908 (vw), 823 (s), 811 (m), 785 (w), 732 (w), 637 (w), 582 (s), 528 (w) cm^{-1}. MS (EI): m/z = 441 [M + H]$^+$, 440, 410 [M – OCH_2]$^+$, 335, 334. $C_{29}H_{28}O_4 \cdot H_2O$ (458.55): C 75.96, H 6.59; found C 76.06, H 6.18.

5,5′,5″,5‴-Methanetetrayltetrakis(2-methoxybenzaldehyde) (3): Tetrakis(4-methoxyphenyl)methane (**2**; 80 mg, 0.18 mmol) and HMTA (500 mg, 3.57 mmol) were dissolved in trifluoroacetic acid (4.5 mL), and the mixture was heated at 100 °C for 18 h. The orange-colored reaction mixture was cooled to room temperature and poured into 0.5 N hydrochloric acid (30 mL) and dichloromethane (25 mL) and stirred at room temperature for 4 h. The layers were separated, the aqueous layer was extracted with dichloromethane (2 × 25 mL), and the combined organic layers were washed with water (2 × 25 mL), saturated $NaHCO_3$ (25 mL), and brine (25 mL), and dried with Na_2SO_4. The solvent was removed in a rotary evaporator to give 100 mg of an off-white solid. Column chromatography (SiO_2, ethyl acetate/petroleum ether, 3:1) and subsequent drying under high vacuum gave 80 mg (80%) of **3** as a colorless solid. M.p. 294–296 °C (dec.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.40 (s, 4 H, ArC*H*O), 7.62 (d, J = 2.4 Hz, 4 H), 7.30 (dd, J = 8.8, J = 2.8 Hz, 4 H), 6.92 (d, J = 9.2 Hz, 4 H) 3.92 (s, 12 H, OCH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.53 (d, CHO), 160.40 (s, Ar*C*-OMe), 138.64, 138.23, 129.11, 123.86, 111.75, 61.99 (s, Ar_4C), 55.78 (q, OCH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3011 (w), 2948 (w), 2875 (w), 2761 (w), 1679 (s), 1604 (s), 1577 (w), 1493 (s), 1461 (w), 1446 (w), 1417 (w), 1392 (m), 1283 (s), 1256 (s), 1202 (w), 1181 (m), 1113 (m), 1016 (m), 919 (w), 834 (w), 809 (w), 731 (vw), 650 (w), 626 (w), 562 (vw), 510 (w) cm^{-1}. MS (CI): m/z (%) = 582 (7), 581 (20) [M + C_2H_5]$^+$, 580 (8), 554 [M + H]$^+$, 553 (100) [M]$^+$, 552 (14), 417 (5), 89 (52), 61 (37). $C_{33}H_{28}O_8$ (552.57): C 71.73, H 5.11; found C 71.60, H 5.16.

5,5′,5″,5‴-Methanetetrayltetrakis(2-hydroxybenzaldehyde) (4): Boron tribromide (1.5 mL, 19 mmol) was added dropwise to a solution of **3** (282 mg, 0.5 mmol) in dry dichloromethane (100 mL) cooled to 0 °C under argon. The reaction mixture immediately turned orange. The mixture was allowed to warm up to room temperature and stirred for 12 h. The mixture was cooled again to 0 °C, water (100 mL) was slowly added, and again the mixture was stirred at room temperature for 4 h. The layers were separated and the organic layer washed with 1 N hydrochloric acid (2 × 100 mL), water (100 mL), and brine (100 mL), and dried with Na_2SO_4. Dichloromethane was removed under reduced pressure to give a red solid. Purification by column chromatography (SiO_2, dichloromethane) gave, after drying, 236 mg (95%) of **4** as a colorless solid. M.p. 280–282 °C. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 10.81 (br. s, 4 H, ArO*H*), 10.21 (s, 4 H, ArC*H*O), 7.37 (d, J = 2.2 Hz, 4 H), 7.12 (dd, J = 8.7, J = 2.2 Hz, 4 H), 6.96 (d, J = 8.7 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 190.81 (d, Ar*C*HO), 159.37 (s, Ar*C*-OH), 138.93, 136.64, 128.64, 121.27, 117.26, 61.20 (s, Ar_4C), 54.86 ppm. IR (KBr pellet): $\tilde{\nu}$ = 3435 (br., m), 2853 (w), 1659 (s), 1621 (m), 1586 (m), 1482 (s), 1375 (w), 1324 (w), 1284 (s), 1236 (m), 1207 (s), 1147 (w), 902 (m), 866 (w), 830 (w), 775 (w), 746 (w), 695 (w), 687 (w), 628 (w), 615 (w), 458 (w) cm^{-1}. MS (CI): m/z (%) = 526 (7), 525 (20) [M + C_2H_5]$^+$, 499 (7), 498 (34), 497 (100) [M + H]$^+$, 496 (17), 375 (9), 139(18), 102 (5), 89 (37), 87 (10), 85 (14), 74 (5), 61 (33). $C_{29}H_{20}O_8 \cdot 0.5CH_2Cl_2$ (538.93): C 65.74, H 3.93; found C 65.99, H 4.00.

Tetrakis(4′-methoxy-1,1′-biphenyl-4-yl)methane (5):[41] Tetrabromide **1** (756 mg, 1.18 mmol) and 4-methoxyphenylboronic acid (788 mg, 5.18 mmol) were suspended in THF (30 mL). An aqueous potassium carbonate solution (2 N, 30 mL), [Pd_2dba_3]·$CHCl_3$ (120 mg, 0.12 mmol, 5 mol-%), and HP(tBu)$_3$BF$_4$ (120 mg, 0.41 mmol) were added. The reaction mixture was heated at 75 °C for 18 h. After cooling the reaction mixture to room temperature,

THF (ca. 200 mL) was added until complete dissolution of the organic material. The layers were separated, the organic layer was washed with water (2 × 100 mL) and brine (100 mL), and dried with Na_2SO_4. After removing the solvent by rotary evaporation, a brownish-green solid remained. Column chromatography (dichloromethane/light petroleum ether, 1:3) gave **5** as a pale-yellow solid. The solid was suspended in methanol (5 mL), collected by suction filtration, and washed with methanol (3 × 5 mL) and light petroleum ether (3 × 5 mL). After drying in vacuo, 760 mg (86%) of **5** remained as colorless solid. M.p. 318–320 °C. ^{1}H NMR (400 MHz, [D$_8$]THF): δ = 7.55 (d, J = 8.8 Hz, 8 H), 7.51 (d, J = 8.4 Hz, 8 H, ArH), 7.37 (d, J = 8.4 Hz, 8 H, ArH), 6.95 (d, J = 8.8 Hz, 8 H, ArH), 3.79 (s, 12 H, OMe) ppm. ^{13}C NMR (100 MHz, [D$_8$]THF): δ = 160.73 (s, Ar*C*-OMe), 146.58 (s), 139.57 (s), 134.10 (s), 132.62 (d), 128.79 (d), 126.61 (d), 115.25 (d), 65.27 (s, Ar$_4$*C*), 55.71 (q, OCH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3029 (m), 3000 (m), 2957 (m), 2906 (m), 2835 (m), 1607 (s), 1580 (m), 1561 (w), 1522 (s), 1494 (vs), 1463 (s), 1441 (s), 1424 (w), 1399 (w), 1289 (s), 1249 (vs), 1210 (m), 1178 (vs), 1111 (w), 1041 (s), 1024 (m), 1014 (m), 1001 (m), 817 (vs), 751 (m), 720 (w), 702 (m), 632 (w), 588 (w), 559 (w), 525 (s) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* (%) = 744 [M]$^+$. $C_{53}H_{44}O_4$ (744.32): C 85.46, H 5.95; found C 85.49, H 5.95.

4′,4‴,4⁗,4⁗⁗-Methanetetrayltetrakis(4′-methoxy-1,1′-biphenyl-3′-carbaldehyde) (6): Tetrakis(biaryl) **5** (750 mg, 1.01 mmol) and HMTA (2.8 g, 20 mmol) were suspended in TFA (25 mL). The reaction mixture was heated at reflux for 18 h. After cooling the reaction mixture to room temperature, the viscous oil was poured into 1 N hydrochloric acid (150 mL), and the mixture was stirred overnight. The precipitate was collected by suction filtration to give 840 mg of a yellow solid. After separation by column chromatography (SiO_2, THF) **6** was obtained as a pale-yellow powder. The powder was washed several times with *n*-pentane and dried in vacuo to give 740 mg (85%) of **6** as an off-white solid. M.p. 296–300 °C. ^{1}H NMR (500 MHz, [D$_6$]DMSO, 373 K): δ = 10.41 (s, 4 H, ArC*H*O), 7.96 ("d", J = 5.0 Hz, 8 H, ArH, two interpenetrating signals), 7.63 (d, J = 8.0 Hz, 8 H, ArH), 7.39 (d, J = 8.0 Hz, 8 H, ArH), 7.31 (d, J = 9.0 Hz, 4 H, ArH), 3.91 (s, 12 H, OMe) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO, 373 K): δ = 188.21 (d, Ar*C*HO), 160.32 (s, Ar*C*-OMe), 144.66 (s), 135.82 (s), 133.25 (d), 131.52 (s), 130.34 (d), 125.10 (d), 124.89 (d), 124.23 (s), 112.97 (d), 63.13 (s, Ar$_4$*C*), 55.61 (q, OCH_3) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3031 (w), 2940 (w), 2862 (w), 1680 (s), 1607 (s), 1580 (w), 1487 (s), 1462 (w), 1442 (w), 1425 (w), 1389 (w), 1305 (vw), 1271 (s), 1247 (m), 1181 (m), 1122 (m), 1049 (w), 1016 (m), 904 (m), 812 (s), 752 (vw), 701 (w), 650 (w), 519 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 879 [M + Na]$^+$, 856 [M]$^+$, 744. $C_{57}H_{44}O_8{\cdot}2H_2O$ (892.33): C 76.67, H 5.42; found C 76.70, H 5.19.

4′,4‴,4⁗,4⁗⁗-Methanetetrayltetrakis(4′-hydroxy-1,1′-biphenyl-3′-carbaldehyde) (7): Boron tribromide (1.2 mL, 15 mmol) was added dropwise to a solution of **6** (500 mg, 0.60 mmol) in dry dichloromethane (100 mL) at 0 °C under argon. The reaction mixture immediately turned red. The mixture was allowed to warm to room temperature and stirred for 3 h. The mixture was cooled again to 0 °C, water (100 mL) was slowly added, and again the mixture was stirred at room temperature for 30 min. The layers were separated, and the organic layer was washed with 1 N hydrochloric acid (2 × 100 mL), water (100 mL), and brine (100 mL), and dried with Na_2SO_4. Dichloromethane was removed in vacuo and the remaining solid diluted in THF and filtered through a plug of silica. After evaporation of the THF, a light-orange solid remained. The solid was suspended in THF (6 mL), collected with a Büchner funnel, and washed with *n*-pentane (3 × 10 mL) to give, after drying in vacuo, **7** as a pale-yellow solid. Yield: 447 mg (97%). M.p. 318–322 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.83 (br. s, 4 H, ArO*H*), 10.30 (s, 4 H, ArC*H*O), 7.94 (d, J = 2.4 Hz, 4 H), 7.86 (dd, J = 8.4, J = 2.4 Hz, 4 H), 7.63 (d, J = 8.4 Hz, 8 H), 7.34 (d, J = 8.4 Hz, 8 H), 7.09 (d, J = 8.8 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 191.42 (d, Ar*C*HO), 160.11 (s, Ar*C*-OH), 145.06, 136.42, 134.33, 130.89, 130.72, 126.79, 125.48, 122.35, 117.87, 63.51 (s, Ar$_4$*C*) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3202 (w), 3029 (w), 2845 (w), 1681 (m), 1655 (s), 1620 (m), 1589 (m), 1477 (s), 1402 (w), 1370 (w), 1323 (w), 1296 (m), 1271 (m), 1223 (m), 1176 (m), 1127 (w), 1015 (w), 960 (w), 907 (m), 819 (s), 770 (w), 757 (m), 739 (w), 695 (w), 679 (w), 587 (w), 531 (m), 468 (m) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 828 [M + 28]$^+$, 800 [M]$^+$. $C_{53}H_{36}O_8{\cdot}3H_2O$ (854.27): C 74.46, H 4.95; found C 74.70, H 4.76.

2-Hydroxy-5-tritylbenzaldehyde (9): Tetrakis(biaryl) **8** (340 mg, 1.00 mmol) and HMTA (190 mg, 1.3 mmol) were suspended in TFA (2 mL). The reaction mixture was heated at 100 °C for 2 h. After cooling the reaction mixture to room temperature, the viscous oil was poured into 1 N hydrochloric acid (15 mL) and dichloromethane (15 mL) and stirred at room temperature for 1 h. The layers were separated, and the organic layer was washed with water (2 × 10 mL) and brine (10 mL), and dried with Na_2SO_4. The solvents were removed by rotary evaporation, and the remaining solid was purified by column chromatography (SiO_2, dichloromethane/petroleum ether, 1:1). After drying in vacuo, 291 mg (79%) of salicylaldehyde **9** remained as a colorless powder. M.p. 184–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.02 (s, 1 H, Ar-O*H*), 9.72 (s, 1 H, ArC*H*O), 7.43 (d, J = 2.4 Hz, 1 H, Ar-2-H), 7.35 (dd, J = 8.8, 2.2 Hz, 1 H, Ar-4-H), 7.18–7.30 (m, 15 H, Ar′-H), 6.90 (d, J = 8.8 Hz, 1 H, Ar-3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8 (d, Ar*C*HO), 160.1 (s, Ar*C*-OH), 146.2, 140.7, 138.7, 134.8, 131.0, 127.8, 126.3, 119.6, 116.9, 64.2 (s, Ar$_3$-*C*-Ar′) ppm. IR (KBr pellet): $\tilde{\nu}$ = 3087 (w), 3052 (w), 3030 (w), 2846 (w), 1659 (s), 1617 (m), 1588 (m), 1478 (s), 1443 (w), 1375 (w), 1350 (m), 1325 (m), 1289 (s), 1236 (m), 1201 (s), 1170 (m), 1130 (m), 1082 (m), 1035 (m), 1010 (w), 1001 (w), 964 (w), 838 (m), 750 (s), 729 (w), 702 (s), 674 (m), 645 (m), 633 (m), 607 (m) cm^{-1}. MS (CI): *m*/*z* (%) = 393 (27) [M + C_2H_5]$^+$, 366 (32) [M + H]$^+$, 365 (100) [M]$^+$, 364 (26), 288 (9), 287 (47), 243 (9). $C_{26}H_{20}O_2$ (364.44): C 85.69, H 5.69; found C 85.86, H 5.69.

Zinc–salphen 11a: Aldehyde **9** (72 mg, 0.20 mmol) and half-imine **10** (104 mg, 0.32 mmol) were suspended in methanol (10 mL) in a screw-capped vial. A solution of zinc acetate dihydrate (72 mg, 0.33 mmol) in methanol (2 mL) was added and the reaction mixture stirred at room temperature for 40 h. The yellow precipitate was collected by suction filtration, washed with methanol (3 × 4 mL), and dried in vacuo to give 130 mg (88%) of **11a** as yellow solid. M.p. >400 °C. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 8.93 (s, 1 H, ArC*H*=N), 8.74 (s, 1 H, Ar′C*H*=N), 7.83 (d, J = 7.9 Hz, 2 H, Ar′-6-H), 7.53–7.02 (m, 21 H, Ar-H), 6.92 (d, J = 8.9 Hz, 1 H, Ar′-4-H), 6.59 (d, J = 8.9 Hz, 1 H, Ar′-3-H), 1.46 [s, 9 H, C(CH$_3$)$_3$], 1.27 [s, 9 H, C(CH$_3$)$_3$] ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 170.63, 170.29, 163.50, 162.53, 146.96, 140.64, 139.97, 139.31, 137.41, 136.38, 133.28, 130.43, 129.64, 127.71, 127.14, 126.54, 125.79, 122.90, 118.17, 118.08, 116.82, 116.76, 116.37, 63.53, 35.20, 33.57, 31.37, 29.62 ppm. IR (KBr pellet): $\tilde{\nu}$ = 3056 (w), 2957 (m), 1614 (s), 1582 (m), 1526 (m), 1469 (m), 1425 (w), 1384 (m), 1360 (w), 1294 (w), 1254 (w), 1194 (w), 1163 (m), 1109 (w), 1036 (w), 972 (w), 923 (w), 835 (w), 793 (w), 748 (m), 702 (m), 625 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 732.7 [M]$^+$, 1565.8 [2 M]$^+$. $C_{47}H_{44}N_2O_2Zn$ (734.24): C 76.88, H 6.04, N 3.82; found C 76.96, H 5.94, N 4.13.

Nickel–salphen 11b: Aldehyde **9** (76 mg, 0.21 mmol) and half-imine **10** (116 mg, 0.35 mmol) were suspended in methanol (6 mL) in a

screw-capped vial. A solution of nickel acetate tetrahydrate (78 mg, 0.27 mmol) in methanol (6 mL) was added and the reaction mixture stirred at room temperature for 46 h. The red precipitate was collected by suction filtration, washed with methanol (3 × 4 mL), and dried in vacuo to give a red solid (160 mg). The solid was redissolved in dichloromethane (20 mL), and overlayered with methanol (60 mL). After complete diffusion of the methanol into the dichloromethane layer, the red precipitate was collected by suction filtration and dried in vacuo to give 126 mg (82%) of **11b** as a red solid. M.p. >400 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1 H, ArC*H*=N), 8.08 (s, 1 H, Ar′C*H*=N), 7.69 (d, *J* = 7.7 Hz, 1 H, Ar′-6-H), 7.62 (d, *J* = 7.9 Hz, 1 H, Ar′-6-H), 7.38 (d, *J* = 2.3 Hz, 1 H, Ar-H), 7.26–7.15 (m, 21 H), 7.08 (d, *J* = 2.3 Hz, 1 H, Ar-H), 7.02 (dd, *J* = 9.1, 2.4 Hz, 1 H, Ar-H), 6.92 (d, *J* = 9.1 Hz, 1 H, Ar-H), 1.44 [s, 9 H, $C(CH_3)_3$], 1.30 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ = 166.26, 164.84, 153.75, 153.56, 146.61, 143.08, 142.66, 140.98, 139.84, 137.01, 133.74, 133.00, 131.11, 130.50, 127.56, 126.88, 126.46, 126.00, 121.16, 119.23, 118.54, 114.70, 114.46, 63.92, 35.59, 34.02, 31.22, 29.38 ppm. IR (KBr pellet): $\tilde{\nu}$ = 3055 (w), 3028 (w), 2957 (m), 2904 (w), 2867 (w), 1616 (s), 1602 (m), 1576 (m), 1523 (m), 1489 (m), 1461 (m), 1425 (w), 1384 (m), 1358 (w), 1335 (w), 1266 (w), 1246 (w), 1198 (w), 1181 (m), 1129 (w), 1110 (w), 1083 (w), 1035 (w), 969 (w), 941 (w), 891 (w), 867 (w), 832 (w), 787 (w), 745 (m), 702 (m), 645 (w), 633 (w), 555 (m), 538 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 726.0 [M]$^+$. $C_{47}H_{44}N_2NiO_2 \cdot 0.5CH_2Cl_2$ (770.03): C 74.09, H 5.89, N 3.64; found C 73.81, H 5.86, N 3.70.

Palladium–salphen 11c: Aldehyde **9** (72 mg, 0.20 mmol) and half-imine **10** (110 mg, 0.34 mmol) were suspended in methanol (6 mL) in a screw-capped vial. A solution of palladium acetate (74 mg, 0.33 mmol) in methanol (6 mL) was added and the reaction mixture stirred at room temperature for 40 h. The orange-brown precipitate was collected by suction filtration, washed with methanol (3 × 4 mL), and dried in vacuo to give 133 mg of an orange-brown solid. The solid was redissolved in dichloromethane (20 mL) and covered with methanol (60 mL). After complete diffusion of the methanol into the dichloromethane layer, a bright-orange precipitate was formed. The precipitate was collected by suction filtration and dried in vacuo to give 90 mg (58%) of **11c** as an orange solid. M.p. >400 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (s, 1 H, ArC*H*=N), 8.34 (s, 1 H, Ar′C*H*=N), 7.87 (d, *J* = 7.9 Hz, 1 H, Ar′-H), 7.79 (d, *J* = 7.8 Hz, 1 H, Ar′-H), 7.52 (d, *J* = 2.0 Hz, 1 H, Ar-H), 7.30–7.08 (m, 21 H, Ar-H), 1.53 [s, 9 H, $C(CH_3)_3$], 1.33 [s, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (126 MHz, $CDCl_3$): δ = 170.03, 167.30, 146.59, 143.88, 141.38, 140.73, 136.81, 135.05, 131.77, 131.72, 131.15, 130.51, 130.47, 128.27, 128.21, 127.60, 127.45, 127.00, 126.94, 126.05, 121.91, 119.87, 119.22, 115.70, 115.39, 63.94, 36.00, 34.02, 31.24, 29.71 ppm. IR (KBr pellet): $\tilde{\nu}$ = 3056 (w), 2957 (m), 1604 (s), 1577 (s), 1513 (s), 1485 (m), 1451 (m), 1385 (m), 1360 (w), 1331 (m), 1244 (w), 1191 (w), 1173 (m), 1132 (w), 1107 (w), 1036 (w), 970 (w), 940 (w), 890 (w), 832 (w), 786 (w), 746 (m), 702 (m), 646 (w), 634 (w), 554 (w), 536 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 773.9 [M]$^+$. $C_{47}H_{44}N_2O_2Pd \cdot 0.5H_2O$ (793.29): C 71.98, H 5.78, N 3.57; found C 71.69, H 5.45, N 4.00.

Tetranuclear Zinc–salphen 13a:[42] Salicylaldehyde **4** (50 mg, 0.10 mmol), half-imine **10** (156 mg, 0.48 mmol), and zinc acetate dihydrate (260 mg, 1.2 mmol) were suspended in dry MeOH (6 mL), and the mixture was stirred at room temperature. After 50 h, a yellow precipitate was collected by suction filtration, washed with dry MeOH (3 × 3 mL), and dried in vacuo (5.1×10^{-1} bar, 100 °C) for 5 h to give 156 mg (73%) of **13a** as an orange solid. M.p. >400 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.92 (s, 4 H, ArC*H*=N), 8.73 (s, 4 H, Ar′C*H*=N), 7.82 (d, *J* = 8.0 Hz, 8 H, Ar′-H), 7.31–7.21 (m, 20 H, Ar-H), 7.10 (d, *J* = 9.1 Hz, 4 H, Ar′′-H), 6.63 (d, *J* = 9.0 Hz 4 H, Ar′′-H), 1.48 [s, 36 H, $C(CH_3)_3$], 1.28 [s, 36 H, $C(CH_3)_3$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 2955 (m), 2905 (m), 2863 (w), 1614 (s), 1581 (s), 1525 (s), 1467 (m), 1424 (m), 1384 (w), 1253 (w), 1194 (m), 1163 (m), 792 (w), 750 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 1976 [M]$^+$.[5] HRMS (MALDI-TOF, DCTB): calcd. for $C_{113}H_{116}N_8O_8Zn_4^+$ 1975.60376; found 1975.61156.

Tetranuclear Nickel–salphen 13b:[42] Salicylaldehyde **4** (50 mg, 0.10 mmol), half-imine **10** (260 mg, 0.80 mmol), and nickel acetate tetrahydrate (260 mg, 0.92 mmol) were suspended in dry DMF (8 mL), and the mixture was stirred at room temperature. After 40 h, a red precipitate was collected by suction filtration, washed with dry DMF (5 × 3 mL), and dried in vacuo (5.1×10^{-1} bar, 100 °C) for 5 h to give 138 mg (70%) of **13b** as a wine-red solid. M.p. >400 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.81 (s, 4 H, ArC*H*=N), 8.77 (s, 4 H, Ar′C*H*=N), 8.23 (d, *J* = 8.2 Hz, 4 H, Ar′-H), 8.12 (d, *J* = 8.4 Hz, 4 H, Ar′-H), 7.47 (d, *J* = 1.5 Hz, 4 H, Ar-H), 7.42 (d, *J* = 1.4 Hz, 4 H, Ar-H), 7.32 (d, *J* = 1.7 Hz, 4 H, Ar-H), 7.29 (t, *J* = 7.5 Hz, 4 H, Ar′′-H), 7.23 (t, *J* = 7.5 Hz, 4 H, Ar′′-H), 7.07 (d, *J* = 9.1 Hz, 4 H, Ar′′-H), 6.80 (d, *J* = 9.0 Hz 4 H, Ar′′-H), 1.39 [s, 36 H, $C(CH_3)_3$], 1.28 [s, 36 H, $C(CH_3)_3$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 2955 (m), 2905 (m), 2867 (w), 1614 (s), 1575 (s), 1520 (s), 1487 (m), 1460 (m), 1425 (m), 1382 (w), 1358 (m), 1336 (w), 1245 (w), 1196 (s), 1182 (s), 1128 (w), 1110 (w), 1044 (w), 942 (w), 920 (w), 892 (w), 862 (w), 842 (w), 803 (w), 787 (w), 742 (m), 712 (w), 638 (w), 552 (w), 536 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 1946.2 [M]$^+$. $C_{113}H_{116}N_8Ni_4O_8 \cdot 2H_2O$ (1984.98): C 68.37, H 6.09, N 5.65; found C 68.34, H 5.89, N 5.66.

Tetranuclear Palladium–salphen 13c:[42] Salicylaldehyde **4** (50 mg, 0.10 mmol), half-imine **10** (260 mg, 0.80 mmol), and palladium acetate (203 mg, 0.90 mmol) were suspended in dry DMF (6 mL), and the mixture was stirred at room temperature. After 60 h, an orange-colored precipitate was collected by suction filtration, washed with dry DMF (4 × 4 mL), and dried in a stream of air to give 300 mg of an orange-colored solid. Recrystallization from CH_2Cl_2/MeOH and then from DMF gave, after drying in vacuo (5.1×10^{-1} bar, 100 °C) for 5 h, 130 mg (61%) of **13c** as bright-orange solid. M.p. >400 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.15 (s, 4 H, ArC*H*=N), 9.06 (s, 4 H, Ar′C*H*=N), 8.40 (d, *J* = 8.7 Hz, 4 H, Ar′-H), 8.33 (d, *J* = 8.5 Hz, 4 H, Ar′-H), 7.65 (d, *J* = 2.0 Hz, 4 H, Ar-H), 7.57 (d, *J* = 2.0 Hz, 4 H, Ar-H), 7.47 (d, *J* = 2.0 Hz, 4 H, Ar-H), 7.39 (t, *J* = 7.7 Hz, 4 H, Ar′′-H), 7.33 (t, *J* = 7.8 Hz, 4 H, Ar′′-H), 7.25 (m, 4 H, Ar′′-H), 7.00 (d, *J* = 9.1 Hz 4 H, Ar′′-H), 1.48 [s, 36 H, $C(CH_3)_3$], 1.31 [s, 36 H, $C(CH_3)_3$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 2955 (m), 2905 (m), 2867 (w), 1605 (s), 1576 (s), 1516 (s), 1487 (m), 1456 (m), 1417 (m), 1385 (w), 1330 (w), 1245 (w), 1192 (s), 1172 (s), 1091 (w), 785 (w), 748 (m), 535 (w) cm^{-1}. MS (MALDI-TOF, DCTB): *m*/*z* = 2142 [M]$^+$. HRMS (ESI) calcd. for $C_{113}H_{116}N_8O_8Pd_4 + H^+$ 2141.51848; found 2141.51866.

Tetranuclear Nickel–salphen 14:[42] Salicylaldehyde **7** (80 mg, 0.10 mmol), half-imine **10** (260 mg, 0.80 mmol), and nickel acetate tetrahydrate (260 mg, 0.92 mmol) were suspended in dry DMF (8 mL), and the mixture was stirred at room temperature for 48 h. After 40 h, a red precipitate was collected by suction filtration and washed with dry DMF (5 × 3 mL). After one night, a second fraction of **14** precipitated from the mother liquor, which was collected by filtration. The combined fractions were dried in vacuo (5.1×10^{-1} bar, 140 °C) for 10 h to give 80 mg (36%) of **14** as a wine-red solid. M.p. >400 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 375 K): δ = 8.89 (s, 4 H, ArC*H*=N), 8.72 (s, 4 H, ArC*H*=N), 8.12 (m, ArH, 4 H), 8.08 (m, 4 H, ArH), 7.98 (d, *J* = 2.3 Hz, 4 H, ArH), 7.71 (dd, *J* = 9.0, 2.5 Hz, 4 H, ArH), 7.64 (d, *J* = 8.6 Hz, 8 H,

ArH), 7.42 (m, 12 H, ArH), 7.38 (d, J = 2.4 Hz, 4 H, ArH), 7.32 (m, ArH, 8 H), 6.92 (d, J = 8.9 Hz, 4 H, ArH), 1.41 [s, 36 H, $C(CH_3)_3$], 1.29 [s, 36 H, $C(CH_3)_3$] ppm. IR (KBr pellet): $\tilde{\nu}$ = 2955 (m), 2905 (m), 2867 (w), 1617 (s), 1601 (s), 1575 (s), 1524 (s), 1506 (m), 1488 (m), 1459 (m), 1425 (m), 1384 (w), 1357 (m), 1336 (w), 1245 (w), 1194 (s), 1179 (s), 1163 (w), 1014 (w), 940 (w), 816 (w), 787 (w), 742 (m), 554 (w), 539 (w) cm^{-1}. MS (MALDI-TOF, DCTB): m/z = 2251.4 $[M]^+$. $C_{137}H_{132}N_8Ni_4O_8{\cdot}2H_2O$ (2289.37): C 71.87, H 5.99, N 4.89; found C 71.88, H 5.80, N 4.87.

Supporting Information (see footnote on the first page of this article): NMR, IR, and mass spectra of all new compounds.

Acknowledgments

The Deutsche Forschungsgemeinschaft (MA4061/4-1) and the Fonds der Chemischen Industrie are gratefully acknowledged for financial support as well as Solvay Fluor GmbH for the donation of chemicals.

[1] a) H. Schiff, *Ann. Chem. Pharm.* **1864**, *131*, 118–119; b) T. T. Tidwell, *Angew. Chem. Int. Ed.* **2008**, *47*, 1016–1020.

[2] a) J.-M. Lehn, *Chem. Eur. J.* **1999**, *5*, 2455–2463; b) S. J. Rowan, S. J. Cantrill, G. R. L. Cousins, J. K. M. Sanders, J. F. Stoddart, *Angew. Chem.* **2002**, *114*, 938–993; *Angew. Chem. Int. Ed.* **2002**, *41*, 898–952; c) R. F. Ludlow, S. Otto, *Chem. Soc. Rev.* **2008**, *37*, 101–108.

[3] a) N. E. Borisova, M. D. Reshetova, Y. A. Ustynyk, *Chem. Rev.* **2007**, *107*, 46–79; b) S. Akine, T. Taniguchi, T. Nabeshima, *Tetrahedron Lett.* **2001**, *42*, 8861–8864; c) A. J. Gallant, M. J. MacLachlan, *Angew. Chem.* **2003**, *115*, 5465–5468; *Angew. Chem. Int. Ed.* **2003**, *42*, 5307–5310; d) C. Ma, A. Lo, A. Abdolmaleki, M. J. MacLachlan, *Org. Lett.* **2004**, *6*, 3841–3844; e) A. J. Gallant, M. Yun, M. Sauer, C. S. Yeung, M. J. MacLachlan, *Org. Lett.* **2005**, *7*, 4827–4830; f) P. D. Frischmann, J. Jiang, J. K.-H. Hui, J. J. Grzybowski, M. J. MacLachlan, *Org. Lett.* **2008**, *10*, 1255–1258.

[4] For reviews, see: a) M. Mastalerz, *Angew. Chem. Int. Ed.* **2010**, *49*, 5042–5053; b) M. Mastalerz, *Chem. Commun.* **2008**, 4756–4758; c) M. Mastalerz, M. W. Schneider, I. M. Oppel, O. Presly, *Angew. Chem. Int. Ed.* **2011**, *50*, 1046–1051; d) D. Xu, R. Warmuth, *J. Am. Chem. Soc.* **2008**, *130*, 7520–7521; e) X. Liu, Y. Liu, G. Li, R. Warmuth, *Angew. Chem.* **2006**, *118*, 915–918; *Angew. Chem. Int. Ed.* **2006**, *45*, 901–904; f) P. Skowronek, J. Gawronski, *Org. Lett.* **2008**, *10*, 4755–4758; g) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. Bradshaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J. Bacsa, A. M. Z. Slawin, A. Steiner, A. I. Cooper, *Nat. Mater.* **2009**, *8*, 973–978; h) N. Christinat, R. Scopelliti, K. Severin, *Angew. Chem.* **2008**, *120*, 1874–1878; *Angew. Chem. Int. Ed.* **2008**, *47*, 1848–1852; i) B. Içli, N. Christinat, J. Tönnemann, C. Schüttler, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2009**, *131*, 3154–3155; j) M. Hutin, G. Bernardinelli, J. R. Nitschke, *Chem. Eur. J.* **2008**, *14*, 4585–4593.

[5] a) S. Akine, T. Nabeshima, *Dalton Trans.* **2009**, 10395–10408; b) S. Akine, T. Taniguchi, T. Nabeshima, *J. Am. Chem. Soc.* **2006**, *128*, 15765–15774; c) R. J. Sarma, J. R. Nitschke, *Angew. Chem.* **2008**, *120*, 383–386; *Angew. Chem. Int. Ed.* **2008**, *47*, 377–380.

[6] a) C. D. Meyer, C. S. Joiner, J. F. Stoddart, *Chem. Soc. Rev.* **2007**, *36*, 1705–1723; b) K. S. Chichak, S. J. Cantrill, A. R. Pease, S.-H. Chiu, G. W. V. Cave, J. L. Atwood, J. F. Stoddart, *Science* **2004**, *304*, 1308–1312.

[7] For a review, see: K. Matsumoto, B. Saito, T. Katsuki, *Chem. Commun.* **2007**, 3619–3627.

[8] For a review, see: a) A. Decortes, A. M. Castilla, A. W. Kleij, *Angew. Chem. Int. Ed.* **2010**, *49*, 9822–9837; b) A. Decortes, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 4580–4582.

[9] S. I. Vagin, R. Reichardt, S. Klaus, B. Rieger, *J. Am. Chem. Soc.* **2010**, *132*, 14367–14369.

[10] a) S. J. Wezenberg, A. W. Kleij, *Angew. Chem.* **2008**, *120*, 2388–2399; *Angew. Chem. Int. Ed.* **2008**, *47*, 2354–2364; b) A. W. Kleij, *Chem. Eur. J.* **2008**, *14*, 10520–10529; c) A. W. Kleij, *Dalton Trans.* **2009**, 4635–4639; d) A. W. Kleij, M. Kuil, D. M. Tooke, M. Lutz, A. L. Spek, J. N. H. Reek, *Chem. Eur. J.* **2005**, *11*, 4743–4750; e) G. Li, W. Yu, Y. Cui, *J. Am. Chem. Soc.* **2007**, *129*, 4582–4583; f) C.-M. Che, C.-C. Kwok, S.-W. Lai, A. F. Rausch, W. J. Finkenzeller, N. Zhu, H. Yersin, *Chem. Eur. J.* **2010**, *16*, 233–247.

[11] R. M. Haak, S. J. Wezenberg, A. W. Kleij, *Chem. Commun.* **2010**, *46*, 2713–2723.

[12] For recent examples, see: a) Z. Zhang, Z. Wang, R. Zhang, K. Ding, *Angew. Chem. Int. Ed.* **2010**, *49*, 6746–6750; b) R. M. Thomas, P. C. B. Widger, S. M. Ahmed, R. C. Jeske, W. Hirahata, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2010**, *132*, 16520–16525; c) P. C. B. Widger, S. M. Ahmed, W. Hirahata, R. M. Thomas, E. B. Lobkovsky, G. W. Coates, *Chem. Commun.* **2010**, *46*, 2935–2937.

[13] a) A. M. Castilla, S. Curreli, N. M. Carretero, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Eur. J. Inorg. Chem.* **2009**, 2467–2471; b) S. Curreli, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *J. Org. Chem.* **2007**, *72*, 7018–7021; c) E. C. Escudero-Adán, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2010**, *12*, 4592–4595.

[14] A. M. Castilla, S. Curreli, E. C. Escudero-Adán, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2009**, *11*, 5218–5221.

[15] a) T. Glaser, M. Heidemeier, H. Theil, A. Stammler, H. Bögge, J. Schnack, *Dalton Trans.* **2010**, *39*, 192–199; b) C. Mukherjee, A. Stammler, H. Bögge, T. Glaser, *Inorg. Chem.* **2009**, *48*, 9476–9484; c) C. Mukherjee, A. Stammler, H. Bögge, T. Glaser, *Chem. Eur. J.* **2010**, *16*, 10137–10149; d) C.-G. Freiherr, V. Richthofen, A. Stammler, H. Bögge, M. W. DeGroot, J. R. Long, T. Glaser, *Inorg. Chem.* **2009**, *48*, 10165–10176.

[16] a) J. H. Chong, S. J. Ardakani, K. J. Smith, M. J. MacLachlan, *Chem. Eur. J.* **2009**, *15*, 11824–11828; very recently, we described the synthesis of similar (triptycene)nickel–tris(salphens) using an air-stable hexaammonium salt as precursor: b) M. Mastalerz, S. Sieste, M. Cenić, I. M. Oppel, *J. Org. Chem.* **2011**, DOI: 10.1021/jo200843r.

[17] a) G. Manecke, W. E. Wille, G. Kossmehl, *Makromol. Chem.* **1972**, *160*, 111–126; b) Y. Dai, T. J. Katz, *J. Org. Chem.* **1997**, *62*, 1274–1285; c) T. Maeda, Y. Furusho, T. Takata, *Chirality* **2002**, *14*, 587–590; d) A. C. W. Leung, J. H. Chong, B. O. Patrick, M. J. MacLachlan, *Macromolecules* **2003**, *36*, 5051–5054; e) T. Maeda, T. Takeuchi, Y. Furusho, T. Takata, *J. Polym. Sci. A: Polym. Chem.* **2004**, 4693–4703; f) A. C. W. Leung, M. J. MacLachlan, *J. Mater. Chem.* **2007**, *17*, 1923–1932; g) A. C. W. Leung, J. K.-H. Hui, J. H. Chong, M. J. MacLachlan, *Dalton Trans.* **2009**, 5199–5210.

[18] a) P. D. Frischmann, J. Jia, J. K.-H. Hui, J. J. Grzybowski, M. J. MacLachlan, *Org. Lett.* **2008**, *10*, 1255–1258; b) G. Salassa, A. M. Castilla, A. W. Kleij, *Dalton Trans.* **2011**, DOI: 10.1039/c1dt10069f; for related supramolecular systems with four metal–salphen units, see, for example: c) K. Chichak, U. Jacquemard, N. Branda, *Eur. J. Inorg. Chem.* **2002**, 357–368; d) S.-S. Sun, C. L. Stern, S. T. Nguyen, J. T. Hupp, *J. Am. Chem. Soc.* **2004**, *126*, 6314–6326; see also refs.[10d,16]

[19] Tetraphenylmethane was first isolated by: M. Gomberg, *Ber. Dtsch. Chem. Ges.* **1897**, *30*, 2043–2047.

[20] For example, see: a) T. J. Zimmermann, O. Freundel, R. Gompper, T. J. J. Müller, *Eur. J. Org. Chem.* **2000**, 3305–3312; b) T. J. Zimmermann, T. J. J. Müller, *Eur. J. Org. Chem.* **2002**, 2269–2279; c) H. Langhals, C. Wagner, R. Ismael, *New J. Chem.* **2001**, *25*, 1047–1049; d) F. A. Neugebauer, H. Fischer, R. Bernhardt, *Chem. Ber.* **1976**, *109*, 2389–2394; e) M. Maus,

R. De, M. Lor, T. Weil, S. Mitra, U.-M. Wiesler, A. Herrmann, J. Hofkens, T. Vosch, K. Müllen, F. C. De Schryver, *J. Am. Chem. Soc.* **2001**, *123*, 7668–7676; f) P. Tinnefeld, K. D. Weston, T. Vosch, M. Coclet, T. Weil, J. Hofkens, K. Müllen, F. C. De Schryver, M. Sauer, *J. Am. Chem. Soc.* **2002**, *124*, 14310–14311; g) W. J. Oldham Jr., R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1998**, *120*, 2987–2988; h) M. L. Renak, G. P. Bartholomew, S. Wang, P. J. Ricatto, R. J. Lachicotte, G. C. Bazan, *J. Am. Chem. Soc.* **1999**, *121*, 7787–7799.

[21] a) U. M. Wiesler, A. J. Berresheim, F. Morgenroth, G. Lieser, K. Müllen, *Macromolecules* **2001**, *34*, 187–200; b) R. E. Bauer, V. Enkelmann, U. M. Wiesler, A. J. Berresheim, K. Müllen, *Chem. Eur. J.* **2002**, *8*, 3858–3864.

[22] R. Rathon, C. C. Burns, I. A. Guzei, *J. Org. Chem.* **2004**, *69*, 1524–1530.

[23] H. L. Aalten, G. van Koten, D. M. Grove, T. Kuilman, O. G. Piekstra, L. A. Hulshof, R. A. Sheldon, *Tetrahedron* **1989**, *45*, 5565–5578.

[24] L. F. Lindoy, G. V. Meehan, N. Svenstrup, *Synthesis* **1998**, 1029–1032.

[25] E. Tzur, A. Ben-Asuly, C. E. Diesendruck, I. Goldberg, N. G. Lemcoff, *Angew. Chem.* **2008**, *120*, 6522–6525; *Angew. Chem. Int. Ed.* **2008**, *47*, 6422–6425.

[26] L. M. Wilson, A. C. Griffin, *J. Mater. Chem.* **1993**, *3*, 991–994.

[27] M.-A. Muñoz-Hernãndez, T. S. Keizer, S. Parkin, B. Patrick, D. A. Atwood, *Organometallics* **2000**, *19*, 4416–4421.

[28] For a review, see: a) A. W. Kleij, *Eur. J. Inorg. Chem.* **2009**, 193–205; b) E. J. Campbell, S. T. Nguyen, *Tetrahedron Lett.* **2001**, *42*, 1221–1225.

[29] A. W. Kleij, D. M. Tooke, A. L. Spek, J. N. H. Reek, *Eur. J. Inorg. Chem.* **2005**, 4626–4634.

[30] The dimer formation of zinc–salphen **11a** complements the results of investigations with similar zinc–salphens reported earlier: M. M. Belmonte, S. J. Wezenberg, R. M. Haak, D. Anselmo, E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans.* **2010**, *39*, 4541–4550.

[31] Data were collected with an Xcalibur Sapphire2 system by using Mo-K_α radiation (λ = 0.71073). The structure was solved by direct methods and refined by full-matrix least-squares methods using SHELXTL-97.[43] All non-hydrogen atoms were refined by using anisotropic thermal parameters. Crystal data for **11a**: T = 110(2) K, $C_{94}H_{88}N_4O_4Zn_2$, M = 1468.42, triclinic space group $P\bar{1}$, a = 9.3987(3), b = 11.4260(5), c = 19.0400(7) Å, α = 97.225(3), β = 98.220(3), γ = 101.553(3)°, V = 1957.4(1) Å^3, Z = 1, $D_{calcd.}$ = 1.246 g cm^{-3}, μ = 0.667 mm^{-1}, 2.85° < θ < 25.25°, reflections collected/unique/observed 22121/7074/6161 [R(int)= 0.0420], data/restraints/parameters 7074/0/475, GOF = 1.082, final R [$I > 2\sigma(I)$]: $R1$ = 0.0379, $wR2$ (all data) = 0.1028, residual density 0.660 and –0.525 e A^{-3}. CCDC-826063 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.

[32] E. C. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Dalton Trans.* **2008**, 734–737; E. C. Escudero-Adán, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Org. Lett.* **2010**, *12*, 4592–4595.

[33] E. Escudero-Adán, J. Benet-Buchholz, A. W. Kleij, *Inorg. Chem.* **2007**, *46*, 7265–7267.

[34] M. E. Germain, T. R. Vargo, B. A. McClure, J. J. Rack, P. G. Van Patten, M. Odoi, M. J. Knapp, *Inorg. Chem.* **2008**, *47*, 6203–6211.

[35] a) J. L. Reddinger, J. R. Reynolds, *Macromolecules* **1997**, *30*, 673–675; b) O. Lavastre, I. Illitchev, G. Jegou, P. H. Dixneuf, *J. Am. Chem. Soc.* **2002**, *124*, 5278–5279; see also ref.[10f]

[36] O. Rotthaus, O. Jarjaves, C. Philhouze, C. P. Del Valle, F. Thomas, *Dalton Trans.* **2009**, 1792–1800.

[37] a) K. Dey, R. L. De, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1530–1532; b) M. R. Mahmoud, S. A. Ibrahim, N. M. Ismail, *Monatsh. Chem.* **1985**, *116*, 167–175.

[38] By using AM1 models of the rigid tetrahedron-shaped compounds, equal distances of all four metal centers to the central quaternary carbon atom are assumed for T_d-symmetric molecules, which results in metal–metal distances of approximately 11.6 Å for **13b** and 18.2 Å for **14**.

[39] M. Mastalerz, H. J. S. Hauswald, R. Stoll, unpublished results.

[40] D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**.

[41] The synthesis of compound **6** by Suzuki–Miyaura cross-coupling has been reported very recently: C. I. Schilling, O. Plietzsch, M. Nieger, T. Muller, S. Bräse, *Eur. J. Org. Chem.* **2011**, 1743–1754.

[42] Owing to the very low solubility of compounds **12a** and **12b**, no satisfactory ^{13}C NMR spectra were recorded, even of saturated solutions of the compounds in deuteriated solvents and with more than 20000 scans.

[43] G. M. Sheldrick, *SHELXTL-97*, Universität Göttingen, Göttingen, **1997**.

Received: May 27, 2011
Published Online: July 25, 2011

