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Reversible Formation and Transmetalation of Schiff-Base Complexes in Subcomponent Self-Assembly Reactions†

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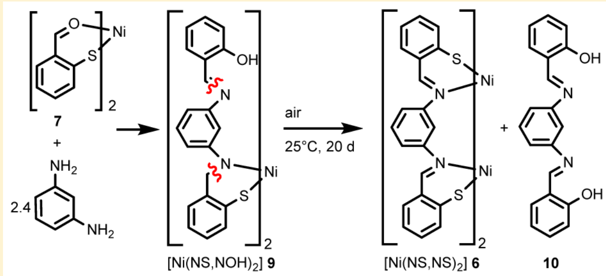
Supporting Information

ABSTRACT: Dinuclear complexes $[Zn_2(NS,NS)_2]$ **3** and $[Ni_2(NS,NS)_2]$ **6** bearing Schiff-base ligands featuring two NS donor groups were obtained in subcomponent self-assembly reactions using nickel or zinc as template metals. Several transmetalation reactions starting from **3** or **6** yielded the complexes $[Pd_2(NS,NS)_2]$ **4** and $[Co_2(NS,NS)_2]$ **5**, and their molecular structures were determined by X-ray diffraction. Starting from the mononuclear complex $[Ni(NS/NOH)_2]$ **9** featuring a coordinated NS Schiff base and a free NOH Schiff base, completely reversible thermodynamically controlled imine bond formation was observed leading to complex $[Ni_2(NS,NS)_2]$ **6** and the free Schiff -base ligand NOH,NOH **10**.



INTRODUCTION

The self-assembly of supramolecular coordination compounds has attracted much interest over the past few decades. This methodology offers the possibility to mimic nature's ability to assemble impressive supramolecular structures.[1] Remarkable results including metal selectivity and recognition in self-assembly reactions have been presented in the past.[2] Recent results include the formation of molecular hosts,[3] molecular traps,[4] catalysts,[5] and helicates.[6] Ligand synthesis and the subsequent reaction with suitable metal ions in self-assembly reactions is often time-consuming,[7] while the recently developed subcomponent self-assembly strategy constitutes an alternative, more efficient approach. Subcomponent self-assembly is based on the reversible condensation of suitable amines with metal-coordinated aldehydes under formation of the thermodynamically most stable metalosupramolecular assembly.[8] The methodology is best described as a template-controlled reversible formation of covalent bonds. For example, in pioneering work Nitschke et al. prepared an unlockable—relockable metal—organic cage, which was capable of tightly binding a hydrophobic guest molecule in aqueous solution.[9]

The subcomponent self-assembly also enables the application of the principles of supramolecular synthesis toward ligands, which are not accessible by conventional organic synthesis. For example, the bidentate thiosalicylaldimine (*o*-mecaptobenzaldimine) donor is not accessible by direct condensation of *o*-mercaptobenzaldehyde with primary amines as this reaction leads to 1,5-dithiocines.[10] However, coordination of 2-thiolatobenzaldehyde to Ni^{II} or Zn^{II} followed by reaction of the mononuclear complexes of type **A** (Figure 1) with a suitable primary diamine yielded dinuclear Schiff-base complexes of type **B**.[11] Using the subcomponent self-assembly it was thus possible to introduce sulfur donors into Schiff-base ligands (hereafter named NS ligands, Figure 1). Combined with the less developed transmetalation reactions,[11,12] subcomponent self-assembly reactions are a powerful tool in supramolecular chemistry.

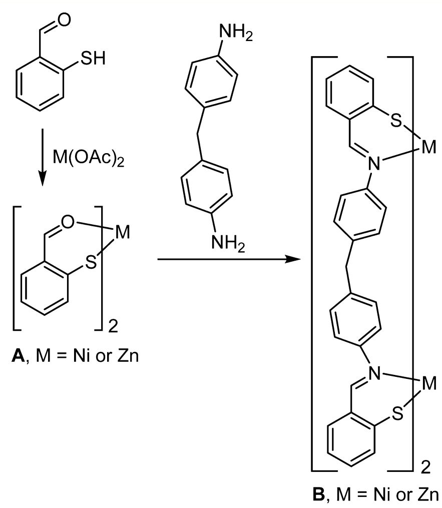


Figure 1. Synthetic strategy for the preparation of complexes bearing thiolato substituted Schiff bases by a subcomponent self-assembly reaction.

Herein, we describe the preparation of several new dinuclear complexes of type **B** (Figure 1). These complexes were prepared using *m*-phenylenediamine as building block for the

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subcomponent self-assembly and featured Schiff-base-derived bidentate NS donor groups. In addition, we present an extension of the ligand synthesis concept by preparation of heterodonor ligands featuring simultaneously thiolato (NS) and hydroxo functionalized (NO) Schiff-base donor groups. Finally, we describe a thermodynamically controlled, completely reversible rearrangement of covalent bonds in a Schiff-base ligand with NS and NO donor groups. The mechanism of this rearrangement is discussed on the basis of time-resolved NMR spectroscopy.

■ RESULTS AND DISCUSSION

We have previously shown that complex zinc complex **2** (obtained in a one-pot reaction at ambient temperature from **1** and $Zn(OAc)_2$) is a suitable starting material for the preparation of dinuclear complexes by the subcomponent self-assembly strategy.[11] We have now reacted complex **2** with *m*-phenylenediamine to obtain the dinuclear complex $[Zn_2(NS,NS)_2]$ **3** bearing two bis(bidentate) NS,NS ligands (Figure 2).

The direct synthesis of the dipalladium complex $[Pd_2(NS,NS)_2]$ **4** by subcomponent self-assembly from a

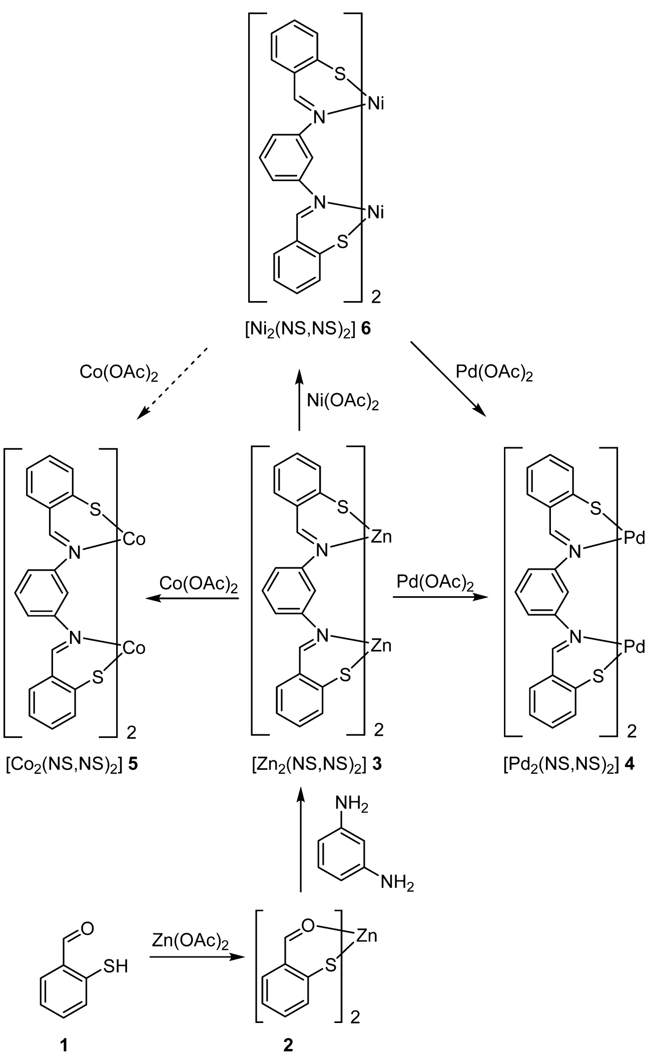

Figure 2. Synthesis of the dinuclear Zn^{II} complex $[Zn_2(NS,NS)_2]$ **3** and transmetalation reactions to give complexes $[Pd_2(NS,NS)_2]$ **4**, $[Co_2(NS,NS)_2]$ **5**, and $[Ni_2(NS,NS)_2]$ **6**.

mononuclear palladium precursor similar to **2** and *m*-phenylenediamine is not possible due to the reduced reactivity of the mononuclear palladium bis(2-thiolatobenzaldehyde) complex toward diamines.[11] However, complex **4** can be obtained by a transmetalation reaction from the dizinc complex $[Zn_2(NS,NS)_2]$ **3** using an excess of $Pd(OAc)_2$ (Figure 2). In addition, complexes $[Co_2(NS,NS)_2]$ **5** and $[Ni_2(NS,NS)_2]$ **6** can be obtained from complex **3** by transmetalation using an excess of $Co(OAc)_2$ or $Ni(OAc)_2$, respectively. To complete the transmetalation series, we also attempted the transmetalation of complex $[Ni_2(NS,NS)_2]$ **6** to complexes $[Co_2(NS,NS)_2]$ **5** and $[Pd_2(NS,NS)_2]$ **4** using an excess of $Co(OAc)_2$ or $Pd(OAc)_2$, respectively (Figure 2). The synthesis of **4** from **6** proceeded within 12 h giving **4** in 75% yield. Interestingly, the reaction of complex **6** with an excess of $Co(OAc)_2$ gave a reaction product producing a MALDI MS spectrum which did not feature the characteristic isotope pattern for the dicobalt complex **5** at m/z = 810 (observed previously for **5** obtained from **3**). Instead, the observed isotope pattern indicated that a mixture of the dinuclear complexes **5** and **6** was obtained (see Supporting Information). Due to the very similar atomic weights of nickel and cobalt both complexes **4** and **6** have a molecular weight of m/z = 810, but the isotope patterns for the two complexes are different, allowing us to distinguish them.

Single crystals for an X-ray diffraction analysis of **5**·DMF have been obtained from the mixture of **5** and **6** by recrystallization from DMF/*n*-hexane or from the transmetalation **3** → **5** followed by recrystallization of the reaction product from DMF/*n*-hexane. Crystals of complexes **3**·2DMF and **6**·2DMF were obtained by recrystallization of the complexes from DMF/*n*-hexane. Crystals of **4**·$2CHCl_3$ were obtained by recrystallization of **4** from a DMF/$CHCl_3$/*n*-hexane solvent mixture. The molecular structures of complexes **3**–**6** obtained by X-ray diffraction studies are depicted in Figure 3.

All four dinuclear complexes feature two metal centers coordinated by two bidentate thiosalicycladimine donor groups from two different NS,NS ligands. Due to the ligand topology, the thiolato donors are always arranged in *cis*-positions (for square-planar coordinated metal centers). The dizinc complex **3** features distorted tetrahedral coordinated metal centers. The metal atoms in dicobalt complex **5** and dinickel complex **6** are coordinated in a slightly distorted square-planar fashion while the platinum atoms in **4** are surrounded in an almost square-planar geometry. The N−M−N bond angles in all complexes are smaller than the S−M−S angles, very likely a consequence of the longer M−S separations compared to the M−N bond distances. The shortest separations between atoms of the bridging rings fall in the range 3.3−3.6 Å which indicates intramolecular (interstrand) $\pi-\pi$-interactions.[13]

Apart from zinc(II), nickel(II) has also been shown to be a suitable template metal for the subcomponent self-assembly reaction.[11] Reaction of **1** with $Ni(OAc)_2$ yields the precursor complex $[Ni(OS)_2]$ **7**.[11] A subsequent reaction of **7** with an excess of *m*-phenylenediamine in the presence of magnesium sulfate in THF, however, yielded the mononuclear complex $[Ni(NS,NH_2)_2]$ **8** (Figure 4) instead of the dinuclear complex $[Ni_2(NS,NS)_2]$ **6** (Figure 2).

During the preparation of complex $[Ni(NS,NH_2)_2]$ **8** only one thiosalicyladimine donor function is generated by Schiff-base condensation at each of the diamines while the second primary amine function is retained. In order to prevent Schiff-

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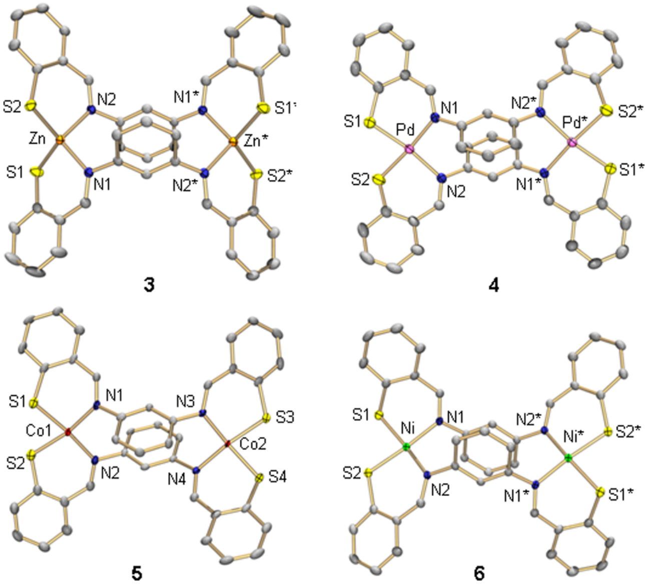

Figure 3. Molecular structures (50% probability ellipsoids) of the complexes **3** in **3**·2DMF (top left), **4** in **4**·2$CHCl_3$ (top right), **5** in **5**·DMF (bottom left), and **6** in **6**·2DMF (bottom right). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg) in **3**: Zn−S1 2.2733(6), Zn−S2 2.2604(6), Zn−N1 2.052(2), Zn−N2 2.036(2); S1−Zn−S2 119.59(3), S1−Zn−N1 97.91(5), S1−Zn−N2 118.62(5), S2−Zn−N1 120.17(5), S2−Zn−N2 98.64(5), N1−Zn−N2 101.75(6). Selected bond lengths (Å) and angles (deg) in **5**: Co1−S1 2.1428(9), Co1−S2 2.1866(8), Co1−N1 1.941(2), Co1−N2 1.952(3), Co2−S3 2.1763(9), Co2−S4 2.1586(10), Co2−N3 1.965(3), Co2−N4 1.964(3); S1−Co1−S2 80.95(3), S1−Co1−N1 96.14(8), S1−Co1−N2 164.32(8), S2−Co1−N1 167.73(8), S2−Co1−N2 90.38(7), N1−Co1−N2 94.97(10), S3−Co2−S4 78.60(4), S3−Co2−N3 89.16(8), S3−Co2−N4 173.14(8), S4−Co2−N3 167.52(8), S4−Co2−N4 94.58(8), N3−Co2−N4 97.69(10). Selected bond lengths (Å) and angles (deg) in **4** [**6**]: M−S1 2.2467(10) [2.1949(6)], M−S2 2.2535(10) [2.1511(5)], M−N1 2.085(3) [1.954(2)], M−N2 2.100(3) [1.950(2)]; S1−M−S2 81.78(4) [80.95(2)], S1−M−N1 93.09(8) [89.50(5)], S1−M−N2 171.09(8) [169.40(5)], S2−M−N1 174.83(8) [165.81(5)], S2−M−N2 89.32(8) [96.27(5)], N1−M−N2 95.81(10) [94.96(6)].

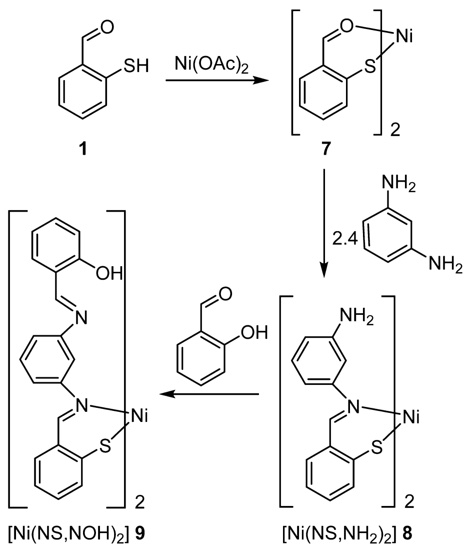

Figure 4. Preparation of the mononuclear complexes [Ni(NS,NH_2)$_2$] **8** and [Ni(NS,NOH)$_2$] **9**.

base condensation at both ends of the *m*-phenylenediamine, it is important to maintain a ratio of **7**:diamine of 1:2.4.

Subsequently, the free amine groups in **8** were reacted in a classical Schiff-base condensation with salicylaldehyde (Figure 4) to give two new uncoordinated bidentate salicylaldimine NOH donor functions in complex **9**. To the best of our knowledge, complex [Ni(NS,NOH)$_2$] **9** constitutes the first example for a ligand featuring two different bidentate heterodonor Schiff-base ligands with an NS and an NO donor set. The combination of different donors in Schiff-base ligands might offer interesting options for the site selective metalation of such ligands, and corresponding studies will be performed in due course.

Complex **9** was characterized by MALDI mass spectroscopy showing the peak with highest intensity at m/z = 720 with the correct isotope distribution calculated for [**9**]$^+$. Furthermore, the ^{1}N NMR spectrum of **9** featured the expected signals for two different imine protons at δ = 9.86 ppm (s, 2H, Ni—N═CH) and δ = 8.44 ppm (s, 2H, N═CH) in addition to the signal of the hydroxyl protons at δ = 12.92 ppm.

Attempts to recrystallize complex **9** from a saturated solution of the complex under nonabsolute conditions produced surprising results. After 2 weeks brown crystals did form from a solution of **9** in DMF/*n*-hexane. However, these brown crystals were not made up from starting material **9** but instead from complex [Ni_2(NS,NS)$_2$] **6** (Figure 5). The formation of crystals of compound **6** was confirmed by MALDI MS spectroscopy (strongest peak at m/z = 810 with correct isotope pattern for [**6**]$^+$) and by X-ray crystallography confirming that the crystals obtained by recrystallization of **9** were identical to those previously obtained by transmetalation of complex **3** with Ni(OAc)$_2$ (complex **6**). The initially used compound **9** was carefully checked before crystallization and was shown to contain no trace of complex **6**. Consequently, [Ni_2(NS,NS)$_2$] **6** must have formed during crystallization of [Ni(NS,NOH)$_2$] **9** from that complex.

In order to learn about the mode of formation of **6** from **9** in the absence of any other reagents, a series of MALDI mass spectra were recorded. The MALDI mass spectrum of a freshly prepared sample of [Ni(NS,NOH)$_2$] **9** was first recorded showing only peaks attributable to [**9**$^+$] (strongest peak at m/z = 720 with isotope distribution of [**9**$^+$]). This sample of **9** was dissolved in DMF/*n*-hexane, and the solution was left standing at ambient temperature without exclusion of moisture for 2 weeks. During this time a small amount of precipitate formed. The supernatant solution was collected and analyzed by MALDI MS spectrometry. The MALDI MS spectrum of the solid obtained from the supernatant solution showed the highest peak at m/z = 810 with an isotope distribution identical to that of [**6**]$^+$ (by comparison with an authentic sample prepared as shown in Figure 2) and another peak at m/z = 317 which can be attributed to compound [**10** + H]$^+$ (Figure 5).

On the basis of these observations, we can assume that a reverse subcomponent self-assembly reaction of [Ni(NS,NOH)$_2$] **9** to give **6** and **10** did proceed during the attempted crystallization over 2 weeks. This rearrangement would involve cleavage of all four imine bonds in **9** and formation of new imine bonds both in **6** and **10** (Figure 5). This appears to be a reasonable proposal given the fact that the whole concept of subcomponent self-assembly is based on the reversibility of the imine bond formation. Imine bond breaking in **9** (NS and NO imine) leads to three fragments as illustrated in Figure 5. These fragments can subsequently recombine

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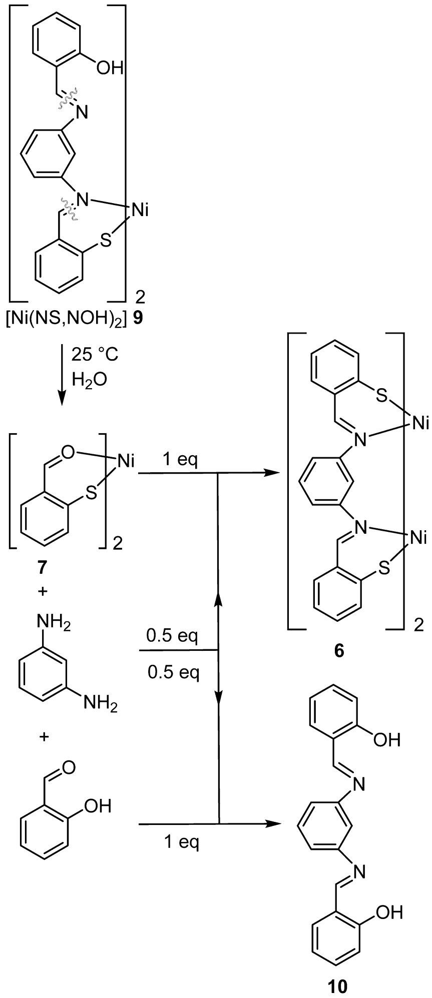

Figure 5. Formation of complex **6** and compound **10** via reverse subcomponent self-assembly reaction from compound [Ni-(NS,NOH)$_2$] **9**.

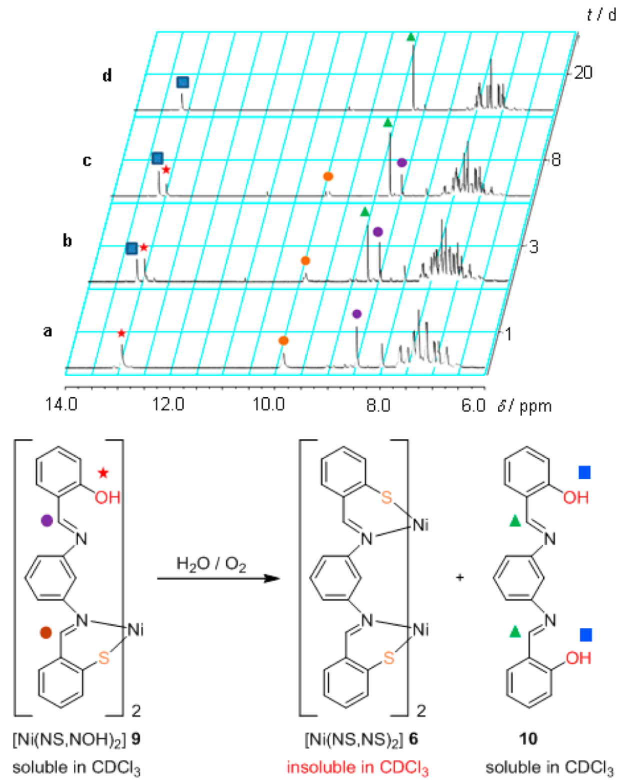

Figure 6. Monitoring of the rearrangement reaction of complex [Ni(NS,NOH)$_2$] **9** to give [Ni$_2$(NS,NS)$_2$] **6** and **10** via time-dependent ^{1}H NMR spectroscopy. ^{1}H NMR spectra of **9** recorded after standing a sample in CDCl$_3$ after dissolving **9** (a), after 3 days (b), after 14 days (c), and after 20 days (d).

under formation of the most stable Schiff bases giving complex **6** and compound **10**. This type of recombination completely consumes the liberated *m*-phenylenediamine which reacts either with complex [Ni(OS)$_2$] **7** to give **6** or with salicylaldehyde to give **10**. The formation of complex **6** is associated with the formation of an equimolar amount of compound **10** as only the formation of **6** liberates the salicylaldehyde needed for the formation of **10**. The driving forces for the whole rearrangement appear to be the general reversibility of the Schiff-base formation and the trend to form the thermodynamically most stable Schiff bases and complexes.

In order to confirm the proposed mechanism for the formation of **6** and **10** by reverse subcomponent self-assembly of **9** we could fortunately make use of the different solubilities of the reaction components. The starting material complex [Ni(NS,NOH)$_2$] **9** and compound **10** are readily soluble in CDCl$_3$, whereas complex [Ni$_2$(NS,NS)$_2$] **6** is completely insoluble in this solvent. These properties allow the design of a time-dependent ^{1}H NMR experiment to establish the mechanism for the reverse subcomponent self-assembly of **9**. In this experiment, mononuclear complex **9** was dissolved in CHCl$_3$ in an NMR tube, and this solution was left standing at ambient temperature for 20 days. ^{1}H NMR spectra of the reaction mixture were regularly recorded (Figure 6).

Figure 6 shows four chronologically recorded ^{1}H NMR spectra of the solution of **9** in CDCl$_3$. The first spectrum (a) was recorded in dry CDCl$_3$ under rigorous exclusion of water in a Young NMR tube. It shows only resonances for the protons of complex [Ni(NS,NOH)$_2$] **9** (the identity and purity of **9** for this experiment was previously also established by MALDI MS spectrometry). After the first spectrum was recorded, the NMR tube was opened up to allow moisture from the air to enter. The presence of water is essential for the subsequent rearrangement reaction. After 3 days the next spectrum (b) was recorded, now showing a new set of resonances belonging to the protons of compound **10** (note that the concurrently formed **6** cannot be observed here as it is insoluble in CDCl$_3$ and precipitates from the solution). As can be seen from Figure 6, the resonances for the protons of the OH groups and of the uncoordinated imine groups in **10** are shifted downfield relative to the equivalent resonances in complex [Ni(NS,NOH)$_2$] **9**. Furthermore, the multiplicity of the signals for the aromatic protons around δ = 7 ppm is reduced over time, which is expected when converting complex **9** with an unsymmetrically substituted central phenylene ring into the symmetrically substituted compound **10**. No resonances assignable to the protons of concurrently formed complex [Ni$_2$(NS,NS)$_2$] **6** were observed due to its insolubility in CDCl$_3$.

Over the next 2 weeks the rearrangement proceeded as indicated by the weakening of the resonances for **9** and a gain of intensity of the resonances for **10**. After 20 days the resonances belonging to the protons of **9** have completely disappeared, and only the resonances for the protons of compound **10** are detectable in the ^{1}H NMR spectrum

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(spectrum **d**) indicative of the completion of the rearrangement. The concurrently formed complex **6** can be isolated from the NMR tube in crystalline form (its identity was subsequently established by recording X-ray diffraction data and comparing these to an authentic sample of **6** obtained via **2** and **3**, see Figure 2).

After having established the rearrangement **9** → **6** + **10** by ^{1}H NMR spectroscopy, we tried to validate our mechanistic proposal further. Therefore, the reversibility of the rearrangement was studied. In addition, we were interested to know if the rearrangement is controlled thermodynamically. As stated before, the rearrangement only proceeds in the presence of water. From a rearrangement reaction of **9**, crystals of complex $[Ni_2(NS,NS)_2]$ **6** were isolated. These crystals were dissolved in DMF, and approximately 2 equiv of salicylaldehyde was added. The resulting reaction mixture was heated to at 100 °C for 48 h without exclusion of air/water (Figure 7).

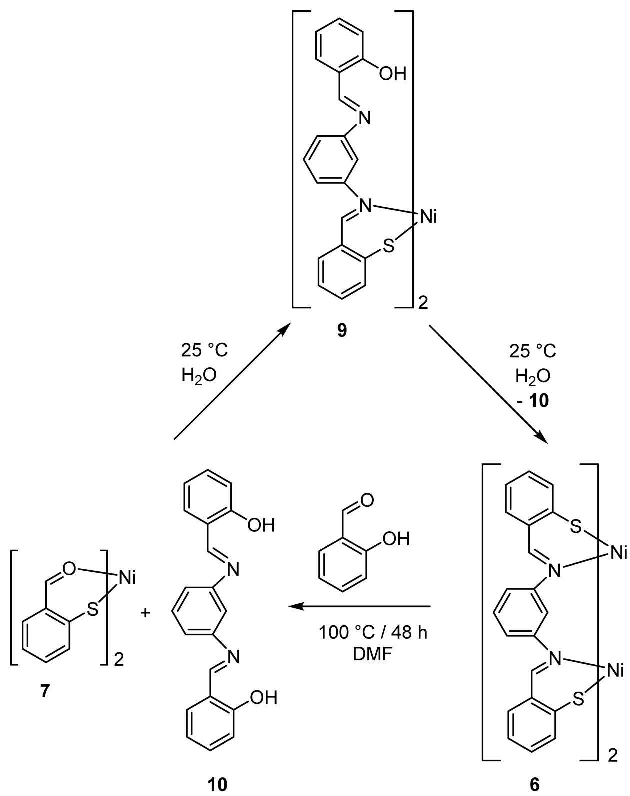

Figure 7. Thermodynamically controlled, reversible formation of imine bonds giving compounds $[Ni(NS,NOH)_2]$ **9**, $[Ni_2(NS,NS)_2]$ **6**, $[Ni(OS)_2]$ **7**, and **10**.

Upon heating of **6** with salicyladehyde complex **7** and compound **10** did form. These two components can react further to give **9** which ultimately rearranged into **6** and **10**. Compounds **6**, **9**, and **10** were identified together with some intermediates of the rearrangement as the major components of the reaction mixture by MALDI mass spectrometry (see Supporting Information). It appears that complex $[Ni_2(NS,NS)_2]$ **6** is the thermodynamically most stable species in the reaction mixture since it is the final product of all rearrangements at ambient temperature in the presence of water. A driving force for the rearrangement leading ultimately to **6** must be the insolubility of this complex in $CDCl_3$ or the DMF/*n*-hexane solvent mixture. Precipitation of **6** shifts the equilibrium toward formation of this complex and the concurrent formation of **10**. Another reason for the preferred formation of **6** is based on the HSAB principle.[14] The relatively soft sulfur donor atoms found in the NS Schiff-base groups in comparison to the harder oxygen donors in the NO Schiff-base groups led to a preferred coordination of the NS donors to the soft nickel(II) centers. This might constitute another reason for the described rearrangement always leading to complex $[Ni_2(NS,NS)_2]$ **6** when performed at ambient temperature in the presence of water.

■ CONCLUSIONS

We present an example for completely reversible imine bond formation which most likely is controlled and directed by thermodynamics. The mechanism for the rearrangement has been established by time-dependent NMR spectroscopy. The rearrangement of the mononuclear complex $[Ni(NS,NOH)_2]$ **9** yields the dinuclear complex $[Ni_2(NS,NS)_2]$ **6** and the tetradentate NOH,NOH Schiff-base ligand **10**. The rearrangement is reversible and can be pushed backward by addition of salicylaldehyde to **6** and heating of the reaction mixture.

■ EXPERIMENTAL SECTION

General Procedures. If not noted otherwise, all reactions were carried out under an argon atmosphere using conventional Schlenk techniques. NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in parts per million downfield from tetramethylsilane or by using the residual protonated solvent as an internal standard. Coupling constants are expressed in hertz. MALDI mass data were obtained with a Bruker Reflex IV spectrometer. The UV–vis data were recorded with a Varian Cary 50 spectrometer. IR data were recorded with a Bruker Vector 22 FT spectrometer. The used solvents were dried following standard procedures and were distilled prior to use. 2-Mercaptobenzaldehyde **1** was prepared by a published procedure.[15]

Complex $[Zn_2(NS,NS)_2]$ 3. Zinc(II) acetate dihydrate (438 mg, 2.00 mmol) was dissolved in MeOH (20 mL), and this solution was added slowly to a solution of 2-mercaptobenzaldehyde **1** (524 mg, 3.80 mmol) in CH_2Cl_2 (20 mL). The reaction mixture was stirred for 12 h. The *m*-phenylenediamine (103 mg, 0.95 mmol) dissolved in CH_2Cl_2 (20 mL) was added dropwise to the solution. After 12 h, a beige precipitate had formed which was isolated by filtration and dried *in vacuo*. Recrystallization (DMF/*n*-hexane, 4:1, v:v) gave yellow crystals which were suitable for an X-ray diffraction analysis. Yield: 485 mg (0.59 mmol, 59%). NMR data could not be recorded due to the poor solubility of the compound in common solvents. MS (MALDI TOF, DCTB): m/z = 824 $[3]^+$. IR (KBr, cm^{-1}): ν = 1707, 1577, 1535, 1459, 1406, 1449, 1070, 972, 753. UV–vis (DMF, nm): ν_{max} = 304, 420.

Complex $[Pd_2(NS,NS)_2]$ 4 by Transmetalation from 3. Complex $[Zn_2(NS,NS)_2]$ **3** (49 mg, 0.06 mmol) was dissolved in DMF (20 mL), and palladium(II)acetate (38 mg, 0.17 mmol) dissolved in MeOH (10 mL) was added dropwise. After stirring of the reaction mixture at ambient temperature for 12 h, *n*-hexane (20 mL) was added, and a red precipitate of complex $[Pd_2(NS/NS)_2]$ **4** formed over several hours. The red solid was isolated by filtration and dried *in vacuo*. Recrystallization (DMF/$CHCl_3$/*n*-hexane, 1:1:2, v:v:v) gave red crystals which were suitable for an X-ray diffraction analysis. Yield: 36 mg (0.40 mmol, 67%). For synthesis of **4** by transmetalation starting from **6**, complex $[Ni_2(NS,NS)_2]$ **6** (32 mg, 0.04 mmol) was dissolved in DMF (20 mL), and palladium(II)acetate (20 mg, 0.09 mmol) dissolved in MeOH (10 mL) was added dropwise. After the reaction mixture stirred at ambient temperature for 12 h, *n*-hexane (20 mL) was added to precipitate the red complex $[Pd_2(NS,NS)_2]$ **4**. The red solid was isolated by filtration and dried *in vacuo*. Yield: 27 mg (0.03 mmol, 75%). NMR data could not be obtained due to the poor solubility of the compound in deuterated solvents. MS (MALDI TOF,

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DCTB): m/z = 906 [**4**]$^+$. IR (KBr, cm^{-1}): ν = 1667, 1577, 1385, 1215, 1158, 1070, 799, 717, 686, 553. UV–vis (DMF, nm): ν_{max} = 400.

Complex [Co_2(NS,NS)$_2$] 5 by Transmetalation from 3. Complex [Zn_2(NS,NS)$_2$] **3** (49 mg, 0.06 mmol) was dissolved in DMF (20 mL), and cobalt(II)acetate (27 mg, 0.15 mmol) dissolved in MeOH (10 mL) was added dropwise. After the reaction mixture stirred at ambient temperature for 12 h, *n*-hexane was added to precipitate the brown complex [Co_2(NS,NS)$_2$] **5**. The brown solid was isolated by filtration and dried *in vacuo*. Yield: 32 mg (0.04 mmol, 67%). For synthesis of **5** by transmetalation starting from **6**, complex [Co_2(NS,NS)$_2$] **5** was synthesized from complex [Ni_2(NS,NS)$_2$] **6** (50 mg, 0.06 mmol), dissolved in DMF (20 mL) by dropwise addition of cobalt(II)acetate (28 mg, 0.16 mmol), dissolved in MeOH (10 mL). After the reaction mixture stirred at ambient temperature for 48 h, the solvent was removed *in vacuo*, and a MALDI mass spectrum of the solid was recorded, which showed an uncharacteristic isotopic pattern, indicating a mixture of complex [Ni_2(NS,NS)$_2$] **6** and complex [Co_2(NS,NS)$_2$] **5**. Recrystallization (DMF/*n*-hexane, 2:1, v:v) gave crystals of complex [Co_2(NS,NS)$_2$] **5** which were suitable for X-ray diffraction analysis. The mass spectrum of the recrystallization product confirmed the presence **5** since it showed the same isotope pattern as an authentic sample of **5** which is different from that of **6** although both **5** and **6** have the same molecular weight of m/z = 810. NMR data could not be obtained due to the poor solubility of the compound in common deuterated solvents. MS (MALDI TOF, DCTB): m/z = 810 [**5**]$^+$. IR (KBr, cm^{-1}): ν = 1670, 1577, 1527, 1481, 1420, 1221, 799, 718. UV–vis (DMF, nm): ν_{max} = 422.

Complex [Ni_2(NS,NS)$_2$] 6 by Transmetalation from 3. Complex [Zn_2(NS,NS)$_2$] **3** (49 mg, 0.06 mmol) was dissolved in DMF (20 mL), and nickel(II) acetate tetrahydrate (37 mg, 0.15 mmol) dissolved in MeOH (10 mL) was added dropwise. After the reaction mixture stirred at ambient temperature for 12 h, *n*-hexane (20 mL) was added to precipitate the dark brown complex [Ni_2(NS/NS)$_2$] **6**. The dark brown solid was isolated by filtration and dried *in vacuo*. Yield: 32 mg (0.04 mmol, 67%). Complex [Ni(NS,NS)$_2$] **6** was also formed by the rearrangement reaction starting with complex [Ni(NS,NOH)$_2$] **9**. After completion of the rearrangement (20 days), complex [Ni_2(NS/NS)$_2$] **6** was removed from the reaction mixture by filtration. Recrystallization (DMF/*n*-hexane, 4:1, v:v) gave crystals which were suitable for an X-ray diffraction analysis. The crystal parameters and MS data of **6** obtained by transmetalation from **3** or by rearrangement of **9** are identical. NMR data could not be obtained due to the poor solubility of the compound in common deuterated solvents. MS (MALDI TOF, DCTB): m/z = 810 [**6**]$^+$. IR (KBr, cm^{-1}): ν = 1588, 1522, 1457, 1217, 1076, 1021, 745, 685. UV–vis (DMF, nm): ν_{max} = 462, 308.

Complex [Ni(OS)$_2$] 7. 2-Mercaptobenzaldehyde **1** (952 mg, 6.90 mmol) was dissolved in methanol (20 mL) and mixed with a solution of nickel(II)acetate tetrahydrate (868 mg, 3.46 mmol) in methanol (20 mL). After the reaction mixture was stirred for 6 h at ambient temperature, a brown solid was isolated by filtration. The precipitate was extracted with CH_2Cl_2 (20 mL). Removal of the solvent *in vacuo* gave a dark brown solid. Yield: 866 mg (2.60 mmol, 75%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 8.98 (s, 2H, O═CH), 7.62 (d, ^3J(H,H) = 8.2 Hz, 2H, Ar—H), 7.55 (d, ^3J(H,H) = 7.9 Hz, 2H, Ar—H), 7.26–7.24 (m, 2H, Ar—H), 7.04 (t, ^3J(H,H) = 7.5 Hz, 2H, Ar—H). ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 189.8 (O═CH), 151.7, 137.8, 133.2, 130.7, 130.6, 122.6 (Ar—C). MS (MALDI TOF, DCTB): m/z = 332 [7]$^+$. UV–vis (DMF, nm): ν_{max} = 439, 308, 270.

Complex [Ni(NS,NH$_2$)$_2$] 8. Complex [Ni(OS)$_2$] **7** (500 mg, 1.50 mmol) was dissolved in THF (20 mL), and $MgSO_4$ (1.0 g) was added. A solution of *m*-phenylenediamine (389 mg, 3.60 mmol) in THF (20 mL) was added dropwise, and the reaction mixture was stirred at ambient temperature for 24 h. The $MgSO_4$ was separated by filtration, and the solvent was removed *in vacuo*. Column chromatography of the residue (SiO_2, CH_2Cl_2/MeOH = 20:1, v:v) gave **8** as a black solid. Yield: 614 mg (1.20 mmol, 80%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 9.43 (s, 2H, N═CH), 7.62 (d, ^3J(H,H) = 8.2 Hz, 2H, Ar—H), 7.26–7.21 (m, 4H, Ar—H), 7.18 (s, 2H, Ar—H), 7.04–6.99 (m, 4H, Ar—H), 6.83 (t, ^3J(H,H) = 7.4 Hz, 2H, Ar—H), 6.45 (d, ^3J(H,H) = 6.8 Hz, 2H, Ar—H), 3.60 (s, 4H, NH_2). ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 161.7 (N═CH), 153.3, 145.8, 139.8, 137.3, 134.4, 132.4, 130.2, 128.1, 123.6, 116.1, 114.2, 113.2 (Ar—C). MS (MALDI TOF, DCTB): m/z = 512 [**8**]$^+$. Anal. Found: C 60.78, H 4.53, N 11.13. Calcd: C 60.83, H 4.32, N 10.92. UV–vis (DMF, nm): ν_{max} = 273.

Complex [Ni(NS,NOH)$_2$] 9. The complex was synthesized from [Ni(NS,NH$_2$)$_2$] **8** (616 mg, 1.20 mmol) dissolved in MeOH (20 mL) by dropwise addition of a solution of salicylaldehyde (0.3 mL, 344 mg, 2.82 mmol) in MeOH (20 mL). The reaction mixture was stirred at ambient temperature for 12 h and subsequently filtered. The solid residue was extracted with CH_2Cl_2 (20 mL), and after removal of the solvent a brown solid was obtained. Yield: 648 mg (0.90 mmol, 75%). ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 12.92 (s, 2H, OH), 9.86 (s, 2H, Ni—N═CH), 8.44 (s, 2H, N═CH), 7.96 (s, 2H, Ar—H), 7.61 (d, ^3J(H,H) = 8.0 Hz, 2H, Ar—H), 7.47 (d, ^3J(H,H) = 7.8 Hz, 2H, Ar—H), 7.39–7.31 (m, 4H, Ar—H), 7.29–7.22 (m, 4H, Ar—H), 7.11 (d, ^3J(H,H) = 8.0 Hz, 4H, Ar—H), 6.96 (d, ^3J(H,H) = 8.4 Hz, 2H, Ar—H), 6.88 (t, ^3J(H,H) = 7.6 Hz, 2H, Ar—H), 6.72 (t, ^3J(H,H) = 7.6 Hz, 2H, Ar—H). ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 163.1 (N═C), 161.6 (Ni—N═C), 161.1 (Ar—C—OH), 153.4, 147.3, 138.8, 138.5, 134.3, 133.6, 132.8, 132.5, 130.5, 128.4, 124.4, 124.1, 121.9, 119.1, 118.8, 118.4, 117.1 (Ar—C). MS (MALDI TOF, DCTB): m/z = 720 [**9**]$^+$. Anal. Found: C 66.18, H 4.15, N 7.58. Calcd: C 66.58, H 4.19, N 7.77. UV–vis (DMF, nm): ν_{max} = 271.

Compound 10. Compound **10** was formed by the rearrangement reaction proceeding from complex [Ni(NS/NOH)$_2$] **9**. After complete rearrangement, complex [Ni_2(NS/NS)$_2$] **6** could be removed by filtration. Removal of the solvent from the filtered solution gave compound **10** as a yellow solid. ^{1}H NMR (400.1 MHz, $CDCl_3$, 300 K): δ = 13.08 (s, 2H, OH), 8.68 (s, 2H, N═CH), 7.49–7.45 (m, 1H, Ar—H), 7.42–7.38 (m, 4H, Ar—H), 7.23–7.21 (m, 1H, Ar—H), 7.19 (s, 2H, Ar—H), 7.07–7.02 (m, 2H, Ar—H), 6.99–6.94 (m, 2H, Ar—H). ^{13}C NMR (100.6 MHz, $CDCl_3$, 300 K): δ = 163.3 (N═CH), 161.2 (Ar—C—OH), 149.7, 133.4, 132.5, 130.3, 119.6, 119.2, 119.1, 117.3, 113.9 (Ar—C). IR (KBr, cm^{-1}): ν_{max} = 3056 (OH), 1622, 1591, 1569, 1496, 1461, 1279, 1156, 1031, 818, 738. MS (MALDI TOF, DCTB): m/z = 317 [**10** + H]$^+$.

X-ray Data Collection and Structure Determination. X-ray diffraction data were collected with a Bruker AXS APEX (Mo Kα radiation) or an AXS SMART (Cu Kα radiation) diffractometer equipped with a rotation anode at 153(2) K using graphite monochromated radiation. Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the Bruker SMART26 program package.[16] Structure solutions were found with the SHELXS-97 package[17] using the heavy-atom method and were refined with SHELXL-97[17] against all F^2.

Crystal Data for 3·2DMF. Formula $C_{46}H_{42}N_6O_2S_4Zn_2$, M = 969.84, yellow block, 0.17 × 0.16 × 0.16 mm^3, a = 10.2801(3) Å, b = 15.3096(4) Å, c = 14.2761(4) Å, β = 101.907(2)°, V = 2198.49(11) Å^3, monoclinic, space group $P2_1/c$, Z = 2, ρ_{calcd} = 1.465 g cm^{-3}, Cu Kα radiation (λ = 1.541 78 Å), μ = 3.481 mm^{-1}, 12 477 intensities measured in the range 8.6° ≤ 2θ ≤ 141.9°, 4039 independent intensities (R_{int} = 0.0465), 3493 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.589 ≤ T ≤ 0.606), refinement of 273 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, R = 0.0384, wR = 0.1065, R_{all} = 0.0432, wR_{all} = 0.1098.

Crystal Data for 4·2CHCl$_3$. Formula $C_{42}H_{30}N_4Cl_6Pd_2S_4$, M = 1144.44, red prism, 0.17 × 0.07 × 0.06 mm^3, a = 9.8549(4) Å, b = 10.5969(4) Å, c = 22.2206(8) Å, β = 94.6070(10)°, V = 2104.84(14) Å^3, monoclinic, space group $P2_1/c$, Z = 2, ρ_{calcd} = 1.806 g cm^{-3}, Mo Kα radiation (λ = 0.710 73 Å), μ = 1.472 mm^{-1}, 24 816 intensities measured in the range 4.0° ≤ 2θ ≤ 61.0°, 6408 independent intensities (R_{int} = 0.0258), 5525 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction (0.788 ≤ T ≤ 0.917), refinement of 262 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms

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on calculated positions, $R = 0.0460$, $wR = 0.1253$, $R_{all} = 0.0537$, $wR_{all} = 0.1301$.

Crystal Data for 5·DMF. Formula $C_{43}H_{35}N_5Co_2OS_4$, $M = 883.86$, red prism, $0.28 \times 0.24 \times 0.22$ mm^3, $a = 16.7647(4)$ Å, $b = 13.2122(3)$ Å, $c = 33.6825(7)$ Å, $V = 7640.6(3)$ Å^3, orthorhombic, space group *Pbca*, $Z = 8$, $\rho_{calcd} = 1.574$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 1.158$ mm^{-1}, 109 631 intensities measured in the range $5.9° \leq 2\theta \leq 62.1°$, 11 894 independent intensities ($R_{int} = 0.1542$), 6994 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction ($0.738 \leq T \leq 0.785$), refinement of 498 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, $R = 0.0547$, $wR = 0.1070$, $R_{all} = 0.1191$, $wR_{all} = 0.1280$.

Crystal Data for 6·2DMF. Formula $C_{46}H_{42}N_6Ni_2O_2S_4$, $M = 956.52$, black plate, $0.10 \times 0.05 \times 0.04$ mm^3, $a = 9.5835(5)$ Å, $b = 11.9723(6)$ Å, $c = 18.4742(9)$ Å, $\beta = 102.3510(10)°$, $V = 2070.6(2)$ Å^3, monoclinic, space group $P2_1/n$, $Z = 2$, $\rho_{calcd} = 1.534$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), $\mu = 1.160$ mm^{-1}, 24 641 intensities measured in the range $4.1° \leq 2\theta \leq 61.0°$, 6309 independent intensities ($R_{int} = 0.0405$), 4893 observed intensities [$I \geq 2\sigma(I)$], empirical absorption correction ($0.893 \leq T \leq 0.955$), refinement of 273 parameters against $|F^2|$ of all independent intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions, $R = 0.0378$, $wR = 0.0871$, $R_{all} = 0.0561$, $wR_{all} = 0.0957$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic date for for **3**·2DMF, **4**·2CHCl$_3$, **5**·DMF, and **6**·2DMF; MALDI MS spectra for all compounds and NMR spectra for compounds **7**−**10**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01334.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

†Dedicated to Prof. Dr. Manfred Scheer on the occasion of his 60th birthday.

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