Supramolecular encapsulation of a rhodium hydroformylation catalyst: a mechanistic study
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Bis-(thiosemicarbazonato) Zn$^{II}$ Complexes as Building Blocks for Construction of Supramolecular Catalysts

Abstract. Herein we report application of bis-(thiosemicarbazonato)Zn$^{II}$ complexes as building blocks in construction of supramolecular transition metal assemblies. We investigated their coordination behaviour towards pyridylphosphine molecules and found these system comparable to those based on Zn(porphyrin) and Zn(salphen) complexes. Additionally, catalytic experiments and in situ high-pressure FTIR study of supramolecular rhodium hydroformylation catalyst assembled using bis-(thiosemicarbazonato)zinc(II) complexes demonstrate their applicability in supramolecular catalysis and their potential for application in other areas of supramolecular chemistry.

2.1. Introduction

Supramolecular chemistry has evolved into a mature field of science and a plethora of fascinating nano-sized structures have been prepared by self-assembly. Whereas the initial focus has been on the generation of the complex nano-sized structures and understanding of the principles involved in their formation, current research is much more associated with the introduction of information (function) into these supramolecules. There is increasing interest in the use of metal-ligand interactions as this strategy provides new opportunities for the introduction of functions. In addition, metal ligand interactions are ideal for the construction of supramolecular assemblies, since they are in general directive and tunable in strength, therefore facilitating the design of structures with controlled geometry and dynamics. The supramolecular structures constructed utilising these interactions include metallo-dendrimers, molecular cages, catenanes and rotaxanes. The latter compounds were shown to be suited for the construction of molecular machines. Also in the area of light harvesting devices such supramolecular structures can potentially be of value. An important research field that has attracted enormous interest in recent years is that of the controlled porous materials and metal-organic frameworks (MOFs). The interest in these materials is fuelled by (potential) application in separation techniques, gas (hydrogen) storage, recognition, sensing and catalysis.

Metalloporphyrins provide versatile building blocks for the construction of all types of supramolecular assemblies and they have also frequently be used for the construction of porous solids materials. Porphyrins are generally flat, rigid, chemically and thermally stable molecules. Moreover, metalloporphyrins have demonstrated catalytic activity in a variety of reactions, and the corresponding metalloporphyrin networks have the potential to act as a shape and size-selective...
heterogeneous catalysts. In addition, they have a rich photochemistry and as such many of these supramolecular assemblies have been used to mimic natural light harvesting systems. In our group metalloporphyrins were used as building blocks for encapsulation of transition metal catalysts. \(^{27,31}\) This resulted in an encapsulated rhodium catalyst that displayed very unusual selectivity in the hydroformylation of 1-octene, next to an increased reactivity of this species with respect to the non-encapsulated analogue. Interestingly, even internal alkenes such as 3-octene could be hydroformylated with reasonable selectivity. This result was unprecedented for these difficult substrates as it required that the catalyst be able to discriminate between an ethyl and an \(n\)-butyl group. \(^{60}\) Recently we also took advantage of the chromophoric character of porphyrins; we assembled zinc(II)-porphyrins to a functionalised bis-(thiolate)-bridged ([2Fe2S]) diiron–based hydrogenase catalyst. This supramolecular complex displayed photo-activity, forming molecular hydrogen upon exposure to light in the presence of a proton source. \(^{108}\)

Since the supramolecular approach to catalyst exploration is very versatile, we aimed at extending the concept to other building blocks. We have demonstrated that the pyridyl analogues of classical BIAN-ligands can be used as the template-ligand, \(^{109}\) and we also have shown that zinc(II)-salphen building blocks can be used analogously to zinc(II)-porphyrins. \(^{52,53,110}\) The salphen building blocks are much easier to prepare and vary structurally, however, they were shown to be subject to trans- and (autocatalytic) demetallation. \(^{111,112}\)

We therefore continued our search for new building blocks and looked into the chemistry of dithiocarbazones (Fig. 2.1.1) and complexes thereof. \(^{65–67,113–115}\) Much to our surprise these building blocks have not yet been studied as molecular building blocks in supramolecular chemistry. In this paper we report the application of the bis-(thiosemicarbazonato)zinc\(^{II}\) (Zn(btsc)) complexes as building blocks in
supramolecular chemistry, i.e. their coordination chemistry with respect to pyridine and pyridylphosphines, as compared to the Zn$^{II}$ building blocks we used previously. We show the Zn(btsc) complexes have properties similar to Zn$^{II}$-porphyrins and -salphens. As an example demonstrating their applicability in construction of supramolecular catalysts, we apply these complexes as building units of rhodium hydroformylation catalysts. With many heteroatoms in the molecule, most notably sulphur, which are potential catalyst poison, the compatibility of the Zn(btsc) complexes with rhodium is an important aspect we looked into. Therefore, formation of the transition metal species under catalytic conditions was closely monitored in situ by high-pressure infrared spectroscopy. We show the formation of the typical bis-phosphine rhodiumhydrido species under hydroformylation conditions. The catalytic activity of these catalysts was evaluated by using a showcase set of terminal and internal alkenes as substrates for hydroformylation. The results of our study suggest a great potential for application of the Zn(btsc) complexes in the area of supramolecular chemistry, which is demonstrated on some examples from the field of supramolecular homogeneous catalysis.

2.2. Results and Discussion

Tetradentate bis-thiosemicarbazone (btsc) (pro)ligands and their metal complexes have been known for over 50 years.$^{65-67}$ The exceptional stability of these complexes, manifested in reversible protonation of the amido side arms, but not demetallation upon treatment with concentrated sulphuric (also phosphoric and perchloric) acid, was exploited early, by using the protonated forms of these complexes as cations in syntheses of complex salts.$^{65,66}$ In addition, when we exposed these complexes to 4-5 equivalents of benzimidazole at 75$^\circ$C, conditions under which Zn(salphen) readily demetallates,$^{112}$ we observed no formation of free ligand or other decomposition signs, even after 18 hours. Besides exceptionally high stability, the (transition) M$^{II}$(btsc) complexes are biologically active and many studies have shown that they display antitumor, antibacterial and antiviral properties.$^{116-118}$ Potential medical application could be found in the affinity of Cu$^{II}$(btsc) complexes towards oxygen-poor (cancer) tissue and applications of M$^{II}$(btsc) complexes (M = Zn, Cu) as tumour marker agents have already been demonstrated.$^{119-126}$

2.2.1. Synthesis. The preparation of M(btsc) complexes is rapid and facile. A typical synthesis protocol consists of two steps: preparation of the (pro)ligand by condensation of a dicarbonyl compound with two thiosemicarbazide molecules, followed by metallation with an appropriate metal salt.$^{127,128}$ Condensation of two different thiosemicarbazides can be performed, leading to dissymmetric M(btsc) complexes which are open to post-synthetic exocyclic modifications. However, it is not a trivial task due to possible side reactions, and strict control of reaction conditions during synthesis is required in order to avoid formation of unwanted products.$^{129}$

For our syntheses we used a slightly modified synthetic procedure as we did not isolate any of the intermediates. The condensation and metallation were performed in a one-pot two step protocol under mild conditions, as shown in Fig.2.2.1. For this initial study three exemplary dissymmetric Zn(btsc) complexes 9–11 with different peripheral substituent sizes were prepared in high yields (70-80%) and purity ($\geq 95\%$, NMR).
2. Zn(BTSC) BUILDING BLOCKS FOR SUPRAMOLECULAR CATALYSTS

![Chemical structures and formulas]

Figure 2.2.1. One-pot two-step protocol for synthesis of dissymmetric Zn(btsc) complexes.

2.2.2. Coordination Studies.

![Phosphorus ligands and coordination equilibrium]

Figure 2.2.2. Phosphorus ligands used in this study and the association equilibrium.

2.2.2.1. Assembly in Solution. The essential element of the ligand-templated approach for encapsulation of transition metal catalysts is coordination of a pyridyl moiety to Zn⁺ centre. The strength of this association is therefore crucial for successful assembly formation, especially for low (catalytic) concentrations the association constant should be high. Association constant $K$ of pyridine to a Zn⁺ building block is often used as a guideline value for the family of similar systems, and the order of magnitude of $K$ is usually more relevant than its exact value. For instance, $K$ values of about $10^3$ and $10^5$ l·mol⁻¹ are typical for pyridine coordination to Zn(porphyrin) and Zn(salphen) complexes, respectively. Precisely determined
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Figure 2.2.3. UV-Vis changes during titration are small, but sufficient to produce well-behaved titration curve (insert), which was used to calculate the association constant: $K = 1.6 \cdot 10^5 \text{M}^{-1}$

binding constants for many similar systems lay in these regions. By performing a UV-Vis titration of the complex 11 with pyridine (see Fig. 2.2.3) we found that their association constant is of the same order of magnitude as Zn(salphen)–pyridine interaction, with $K = (1.6 \pm 0.1) \cdot 10^5 \text{ l/mol}^{-1}$. This high K value makes the Zn(btsc) complexes interesting for application as supramolecular building units.

Figure 2.2.4. Solid state structures of the assemblies. Thermal motion ellipsoids drawn at 50% probability. H atoms and co-crystallised solvent molecule (toluene in 9·L3) removed for clarity. Colour legend: C white, N blue, S yellow, P orange and Zn magenta.

2.2.2.2. Assemblies in the Solid State. To further confirm the coordination of phosphine-pyridyl ligands to these Zn$^{II}$ building blocks, the coordination complexes

\footnote{The ligands L2–L4, Fig. 2.2.2a, are routinely used as templates for construction of supramolecular transition metal catalysts. The position of the nitrogen donor in L2 and L3, allows creation of}
were crystallized from toluene solution by gas-phase hexane diffusion. The crystal structures of assemblies of complex 9 with 3- and 4-(diphenylphosphino)-pyridine (L2 and L3, Fig. 2.2.2a) show axial coordination of pyridyl moiety to the Zn\textsuperscript{II} centre, which adopts square-pyramidal geometry, bending slightly out of the SNNS–plane (see Fig. 2.2.5). Importantly, the lone pair of either phosphorus atoms is not involved in coordination, and therefore could be used for coordination to (soft) transition metals.

An interesting feature of both assemblies is formation of dimeric super-structures via two N − H · · · S bonds per dimeric unit, similar to Zn(btsc) dimers Alsop et al. reported.\textsuperscript{134} The N-S distances of atoms involved in hydrogen bonding are typical for such structure (3.463(4) Å (9·L3) and 3.702(11) Å (9·L2)).\textsuperscript{134} The dimers are shown in Fig. 2.2.5, which also displays the stacking of Zn(btsc) complexes in the solid state. The distance between the Zn-N-C-C-N planes of the two stacking units is around 3.5 Å (3.560(4) Å in 9·L2 and 3.5295 (18) Å in 9·L3), suggesting existence of π − π interactions, not unusual in flat, aromatic molecules.\textsuperscript{135–141} In these dimers, the Zn(btsc) complexes are almost perfectly coplanar, while the pyridylphosphine moieties coordinate to Zn\textsuperscript{II} centres on opposite sides of the plane defined by two Zn(btsc) complexes. This 2:2 assembly is strikingly similar to the 1:2 assembly Kuil et al. reported, where two L2 molecules coordinate to Zn centres on opposite sides of a (bis-Zn\textsuperscript{II})-salphen complex.\textsuperscript{131} The zinc-zinc distance in the current structures are 8.78 Å (9·L3) and 9.19 Å (9·L2), which is similar to the qualitatively different steric bulk upon coordination of a Zn\textsuperscript{II} complex to N. In addition, the electronic effects of N in these positions influence – not-equally – the electronic properties of P, creating slight differences in electron density on the transition metal during catalysis. These electronic differences might be reflected in the catalytic activity. The ortho-pyridyl analogues of these ligands were not used due to their sterically hindered and therefore weak, binding of Zn\textsuperscript{II} building blocks.
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Zn· · · Zn distance in the 1:2 assembly. However, there is no evidence that such structures form N – H · · · S bonds in solution, and we did not observe any effect typical for formation of a supramolecular bidentate ligand on a bis-Zn\textsuperscript{II} platform in asymmetric hydroformylation of styrene, as it was described by Kuil.\textsuperscript{131}

\[
\begin{align*}
\text{(a) incubation} & \\
\text{(b)} & 
\end{align*}
\]

\textbf{Figure 2.2.6.} Top: Activation of a rhodium hydroformylation catalyst (incubation). Below: Hydroformylation of 1-, trans-2- and trans-3-octene.

2.2.3. \textit{In situ} High-Pressure Infrared Spectroscopy. The assemblies of Zn(btsc) complexes with L2-L4 are essentially monodentate ligands, with unconventional steric bulk remote from the phosphorus atom. They are also electronically different from a typical monodentate ligand, triphenylphosphine (L1), so it was interesting to see what effect of these differences would have on the catalyst under hydroformylation conditions.\textsuperscript{ii}

In a typical hydroformylation experiment Rh(acac)(CO)\textsubscript{2} and the ligands are mixed \textit{in situ} to form the active species (Fig. 2.2.6a).\textsuperscript{iii} We monitored the formation of rhodium supramolecular catalyst from Rh(acac)(CO)\textsubscript{2} as precursor, the template ligand L4, and the Zn(btsc) complex\textsuperscript{iv} 9 using infrared spectroscopy.\textsuperscript{142,143}

\textsuperscript{ii}Typically 20 bar syngas, CO/H\textsubscript{2}=1:1.
\textsuperscript{iii}Catalyst activation during the incubation under syngas comprises a set of reactions schematically shown in Fig. 2.2.6a. In such reaction mixture of rhodium hydride isomers with two phosphine ligands are formed. In one isomer, P ligands occupy two equatorial coordination sites on trigonal-bipyramidal rhodium centre (eq-eq or ee, Fig. 2.2.6a) whereas in the other rhodium complex one P ligand coordinate in equatorial, and the other P ligand in apical fashion (eq-ap or ea, Fig. 2.2.6a).\textsuperscript{14} Each of these isomers produces two characteristic CO-bands in infrared spectrum, leading to total of four bands, when both isomers are present in solution.

\textsuperscript{iv}no nitrogen base was added, what is required with ZnTPP and Zn(salphen) complexes in order to prevent demetallation.
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Figure 2.2.7. Left: the in situ FT-IR spectrum (left) of the supramolecular rhodium catalyst showing the rhodium carbonyl region. The the four bands indicate presence of the ee and ea rhodium isomers in the solution (the weak band at 2135 cm\(^{-1}\) is the free CO; p = 20 bar, CO/H\(_2\) = 1 : 1, T = 40\(^\circ\)C).
Right: The molecular model of the ee isomer optimised using PM3 method. Although bulky, the supramolecular ligand allows formation of bis-ligated rhodium species. Colour legend: C black, H white, O red, N blue, P orange, S yellow, Zn dark violet, and Rh magenta.

The IR spectrum is similar to that of the triphenylphosphine analogue. Four bands of similar intensities were observed at 2071, 2056, 2005 and 1970 cm\(^{-1}\) are observed, indicating that the ee and ea isomers are formed in approximately equimolar amounts. The shoulder at ca. 1920 cm\(^{-1}\) might be the Rh–H stretch, which is rarely observed.\(^{21}\) For comparison, application of ZnTPP instead of Zn(btsc) as the template, led exclusively to the formation of mono-ligated complexes because the assembly L4·(ZnTPP)\(_3\) is so large, that only one phosphorus can coordinate to rhodium.\(^{27}\) This indicates that the significant difference in size between the Zn(btsc) and ZnTPP is reflected in the coordination mode, allowing formation of bis-phosphine rhodium species by application of Zn(btsc), while a mono-phosphine rhodium species was formed when ZnTPP was used. The molecular modelling figure of the the ee isomer, Fig. 2.2.7b, shows that in the bis-phosphine rhodium species there are no significant steric hindrances between the Zn(btsc) building blocks. Numerous phosphine conformations and large rotational freedom around N-Zn bond convey considerable flexibility to the assembly, allowing a facile avoidance of steric crowding.

2.2.4. Catalysis. That these rhodium species are also active catalysts for hydroformylation was confirmed by addition of substrate to the mixture in the IR autoclave. Injection of 1-octene into the autoclave triggered immediate start of hydroformylation, with initial turnover frequency (TOF) of about 60 h\(^{-1}\), which is significantly faster than observed with triphenylphosphine (4–15 h\(^{-1}\)), but still slower than with ZnTPP (∼130 h\(^{-1}\)) under similar conditions.\(^{27,31,52,54,110}\) The four carbonyl bands of the rhodium species do not change during catalysis, showing that
the rhodium hydride complexes represent the resting state of the catalyst. This, together with the rate order in (respect to) substrate of 1 (see insert in Fig. 2.2.8a), indicated that the hydroformylation follows type I kinetics.

A more extensive set of catalytic experiments were performed using Zn(btsc) complexes 9-11, ligands L1-L4, and substrates shown in Fig. 2.2.6b. As expected, the conversions of terminal internal alkenes were higher than those of internal alkenes for all catalytic systems. Additionally, the PPh$_3$-based rhodium catalysts display lower conversions than those with pyridyl-Zn(btsc) moieties. Interestingly, the conversion is higher if more phenyl groups on P are replaced by pyridyl–Zn(btsc) motifs, see Fig. 2.2.8b.

Unexpectedly, the presence of three equivalents of Zn(btsc) 9 in a hydroformylation experiment using L1, which has no positions for coordination of Zn$^{II}$, also led to increased conversion (entry 2 in Tab. 2.2.1). Importantly, this experiment shows clearly that the Zn(btsc) complexes do not poison the catalyst. In fact, even as spectators they accelerate the catalysis slightly, and significantly if they participate as building blocks of the supramolecular catalysts. The origin of this effect is not clear yet, however, it is possible that the Zn(btsc) complexes contribute to electron-depletion of the rhodium centre, making it more catalytically active. In the experiment 2 (entry 2, Tab. 2.2.1), the Zn$^{II}$ centre may coordinate to O of a Rh-associated carbonyl functionality,$^{vi}$ withdrawing electron density via the $\sigma$ bonds. In experiments with Zn(btsc)-L2 to L4, the pyridylphosphine itself is electron-poorer than PPh$_3$ due to electronegative nitrogen in the ligand; additionally, coordination of Zn(btsc) complexes to N leads to further electron-depletion.

$^v$In type I kinetics, reaction rate order in substrate is 1, and the rate-limiting, as well as the rate-determining step are early in the catalytic cycle. In the type II kinetics, the rate order in substrate is zero and hydrogenolysis is the rate-limiting step.$^{11,12}$.

$^vi$CO coordinated to Rh or, less probable, CO of the Rh–acyl moiety.
Table 2.2.1. Hydroformylation of terminal and internal octenes.

<table>
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<th>Entry</th>
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<th>Conv. (%)</th>
<th>Iso. (%)</th>
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<th>P2</th>
<th>P3</th>
<th>P4</th>
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Conditions: \([\text{Rh}]= 0.70 \cdot 10^{-3} \text{ mol l}^{-1}, [\text{P}]/[\text{Rh}]= 5.0, [\text{Zn}]/[\text{equiv. pyridyl group}]= 1.0, [1-octene]/[\text{Rh}]= 1000, 16 \text{h}; [\text{trans}-2-octene]/[\text{Rh}]= [\text{trans}-3-octene]/[\text{Rh}]= 500, 24 \text{h}; T= 40^\circ \text{C}, \text{p}= 20 \text{bar}, \text{CO}/\text{H}_2= 1 : 1. \) Reaction mixture quenched by cooling and addition of tributylphosphite, diluted with CH\(_2\)Cl\(_2\) and analysed by GC.

of the ligand and rhodium centre. Generally accepted\(^{11,12}\) effects of reduced back-donation from Rh to coordinated CO or alkene are:

- facilitated CO dissociation from the rhodiumhydrido resting state and entry of the catalyst into the catalytic cycle
- weaker back-donation from Rh to the coordinated alkene, facilitating rotation around Rh–alkene σ-bond and lowering the hydride migration barrier.

These effects directly cause higher catalytic activity, but also higher alkene isomerisation rate. This is well documented in the case of phosphites, which display both effects (increase of isomerisation and hydroformylation rate).\(^{11,12,61–64,144–147}\) In our case, the electronic effects are much smaller than in the experiments in which
phosphines are compared to phosphites. Therefore, we observed “only” fourfold increase in TOF: 60 vs. 15 h\(^{-1}\) with L\(4\)·\(9\)\(_3\) and PPh\(_3\), respectively. Decreased back-donation to the anti bonding CO-orbitals leads to stronger CO bond of the coordinated CO molecules and as a consequence to higher frequencies of the CO vibrations in the IR spectrum.\(^{14}\) Indeed we find this experimentally: the HP-IR spectrum of the PPh\(_3\)-based rhodium catalyst displays bands 15–30cm\(^{-1}\) lower than the supramolecular catalyst.

\[
\text{PPh}_3: \text{2055, 2030, 1989 and 1941cm}\^{-1} \\
\text{L}\_4\cdot\text{9}_3: \text{2071, 2056, 2005 and 1970cm}\^{-1}.
\]

Similar wavenumber differences were previously reported with systems using xantphos ligands bearing substituents with variable electron-withdrawing properties.\(^{14}\)

The selectivity of the current encapsulated catalyst is virtually identical to PPh\(_3\)-based rhodium catalysts. Thus, the application of Zn(btsc) building blocks for supramolecular rhodium catalysts leads to increased conversions in hydroformylation of terminal and internal octenes, while preserving the selectivity typical for PPh\(_3\)-based catalysts.

2.3. Summary and Conclusions

We have studied the application of a small set of bis-(thiosemicarbazonato)-Zn\(^{II}\) complexes as building blocks for construction of supramolecular complexes, in particular as building blocks that associate to ligand-templates to encapsulate transition metal complexes for catalysis. The coordination behaviour of these complexes is similar to that of Zn(salphen), with pyridine-Zn(btsc) association constant of \(K = 1.6 \cdot 10^5\cdot\text{mol}^{-1}\), two orders of magnitude higher than those displayed by related Zn\(^{II}\)(porphyrin)-pyridine systems. In addition, the current complexes are significantly more stable than the Zn(salphen) complexes, especially concerning demetallation under acidic conditions.

Under syngas atmosphere, the supramolecular ligands formed by these bis-(thiosemicarbazonato)Zn\(^{II}\) complexes and tris-pyridyl-phosphine ligand building block react with a rhodium precursor giving active hydroformylation catalysts that display type I kinetics. According to the \textit{in situ} HP-IR spectroscopy, the encapsulation does not lead to phosphine dissociation as bisphosphine complexes are formed. The selectivity is typical for PPh\(_3\)-based rhodium catalysts, however, the activities are significantly higher than those observed with PPh\(_3\). The differences in reactivity are likely due to electronic properties, as the supramolecular ligands are more electron-deficient than PPh\(_3\).

We have thus successfully demonstrated applicability of Zn(btsc) complexes as building blocks for construction of supramolecular ligand assemblies and rhodium hydroformylation catalysts thereof. A particularly interesting aspect, and a great potential of these complexes, is their structural variability and possibility for post-synthetic modifications. The opportunity to access a stable building block that is easy to modify makes these building blocks very attractive for further exploration in supramolecular chemistry, also including applications other than catalysis.

2.4. Experimental Section

Solvents used for the syntheses of Zn(btsc) complexes and their precursor compounds were obtained from Biosolve and were not further purified. Solvents used in catalytic, spectroscopic (HP-FTIR, UV-Vis) and crystallisation experiments were
dried and freshly distilled prior to use: toluene and hexane were distilled over Na, \( \text{CH}_2\text{Cl}_2 \) over CaH\(_2\). All deuterated solvents except dmso were dried and degassed by the freeze–pump–thaw technique and kept under 3–4 Å molecular sieves. Reagents 1-3, 7, 8, L1 and Zn(\( \text{CH}_3\text{COO} \))\(_2 \cdot 2\) \( \text{H}_2\text{O} \) were purchased from Aldrich and used without further purification. Substrates for catalysis and high-pressure IR were degassed by dinitrogen bubbling and filtered over short plug of alumina prior to use. Phosphine ligands were prepared according to the previously published procedures.\(^{149}\) NMR spectra were acquired on the Varian Mercury-VX 300, Bruker DRX300 (\( ^1\)H at 300 MHz, \( ^{31}\)P at 100 MHz, and \( ^{13}\)C at 75 MHz), and Bruker ARX400 (\( ^1\)H at 400 MHz, \( ^{31}\)P at 125 MHz, and \( ^{13}\)C at 100 MHz). The resonances are referenced to solvent itself as internal standard and are reported in parts per million (ppm). Mass spectrometry (MS) measurements were performed using fast atom bombardment (FAB+) ionisation mode. IR spectra were recorded on the Nicolet Nexus 670 FT-IR spectrometer operated by Omnic 6.2 Software; UV-Vis measurements were performed on the Hewlett-Packard 8453 spectrometer; Gas chromatography (GC) analysis were done on the Shimadzu GC-17A chromatograph equipped with an FID detector using a 30 mm long column with 0.32 mm diameter and dimethylsiloxane cross-linked phase of 3 \( \mu \)m thickness. Catalytic experiments were performed in mini-4-autoclaves connected to the same high-pressure line, allowing all four reactions to be run under the same pressure. Before each run the autoclaves were evacuated, flushed with nitrogen, and tested for leaks at ca. 35 bar syngas. Molecular graphics images were produced using the UCSF Chimera package from the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco.\(^{150}\)

### 2.4.1. Syntheses

#### 2.4.1.1. Compound 5.

It was prepared as described by Cowley et al.\(^{127}\) Thiosemicarbazide 3 (1.00 g, 9.51 mmol) was dissolved in water (17 ml) and treated with 5.5 ml conc. HCl at 10°C in a 100 ml round-bottom flask. Cooled solution of diketone 1 (1.0 ml, 11.85 mmol) in water (20 ml) was added dropwise under vigorous stirring. White bulky precipitate formed immediately. After 2 hours of stirring under ice cooling the product was collected by filtration, washed twice with 20 ml cold water, once with 15 ml of cold diethyl ether and dried in air. Yield: 1.33 g (81%) of white powder. NMR analysis of the product showed \( \geq 95\% \) purity and it was used further without additional purification.

\(^1\)H NMR (300 MHz, dmso-d\(_6\), 25°C, \( \delta \)): 10.63 (s, 1H, N\( \text{H} \)), 8.61 (s, br, 1H, CH\(_3\)NH), 3.04 (s, br, 3H, CH\(_3\)NH), 2.40 (s, 3H, CH\(_3\)CO), 1.94 (s, 3H, CH\(_3\)CN). \(^{13}\)C\({}^1\)H NMR (75 MHz, dmso-d\(_6\), 25°C, \( \delta \)): 197.2 (C=O), 178.6 (C), 145.2 (C), 31.1 (CH3), 24.5 (CH3), 9.7 (CH3). MS (FAB+): m/z = 173.0491 found, calculated 173.0600.

#### 2.4.1.2. Compound 6.

It was prepared analogously to compound 5. Thiosemicarbazide 4 (2.51 g, 15.00 mmol) was partially dissolved in water (60 ml) and treated with 0.5 ml 6 M HCl at 10°C in a 200 ml round-bottom flask. Cooled solution of 1 (1.65 ml, 18.75 mmol) in water (30 ml) was added dropwise to solution of 4 under vigorous stirring. White bulky precipitate formed immediately. More water (50ml) was added to facilitate stirring. After 1.5 hours of stirring under ice cooling, the product was collected by filtration, washed twice with 30 ml cold water, once with 25 ml of cold diethyl ether and dried in air. Yield: 3.23 g (91%) of white powder. NMR analysis showed the product purity \( \geq 95\% \). It was used further without additional purification.

\(^1\)H NMR (300 MHz, dmso-d\(_6\), 25°C, \( \delta \)): 10.34 (s, 1H, NH),
9.82 (s, 1H, NH), 7.59 (d, \(^3J = 7.6\) Hz, 2H, H\(_{Ar}\)), 7.36 (t, \(^3J = 7.4\) Hz, 2H, H\(_{Ar}\)), 7.15 (t, \(^3J = 7.4\) Hz, 1H, H\(_{Ar}\)), 1.99 (s, 3H, CH\(_3\)), 1.07 (s, 3H, CH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (75 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 175.7 (C=O), 152.1 (C), 138.4 (C), 127.5 (2C), 127.4, 124.3 (3C), 24.5 (CH\(_3\)), 17.4 (CH\(_3\)). MS (FAB+): m/z = 399.0663 found, calculated 399.0404.

2.4.1.3. Compound 7. This compound was prepared as described by Bost and Smith.\(^{151}\) Benzil, 2 (2.00 g, 9.51 mmol), and thiosemicarbazide 4 (1.60 g, 9.51 mmol) were treated with 1 ml of glacial acetic acid in ethanol under reflux for 2 hours. A creamy precipitate formed upon cooling, which was collected by filtration, washed with ice-cold ethanol (3×10 ml) and dried in vacuo. Yield: 2.33 g (86%) of fine white powder. NMR analysis showed ≥95% purity. The product was used further without additional purification. \(^1\)H NMR (300 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 12.23 (s, 1H, NH), 8.45 (s, 1H, NH), 7.62 (d, \(^3J = 7.4\) Hz, 2H, H\(_{Ar}\)), 7.39 – 7.14 (m, 12H, H\(_{Ar}\)), 6.11 (d, \(^3J = 7.4\) Hz, 1H, H\(_{Ar}\)). \(^{13}\)C\(^{1}\)H NMR (75 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 170.8 (C=O), 146.1, 140.9, 138.8, 134.3, 132.1, 131.5, 130.4, 129.6, 129.5, 128.7, 128.1, 127.8 (2C), 127.7 (4C), 127.6, 127.1, 126.5 (C). MS (FAB+): m/z = 359.1096 found, calculated: 359.1100.

2.4.1.4. Complex 9. This complex was prepared according to procedure described by Cowley et al. Compound 8 (253 mg, 2.12 mmol) was dissolved in tetrahydrofuran (thf) and treated with glacial acetic acid (0.2 ml) for ca. 20 minutes. 6 (500 mg, 2.12 mmol) was added to the solution and the mixture was stirred at room temperature next 3 hours. Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (559 mg, 2.54 mmol) was dissolved in 15 ml methanol and then added to the reaction mixture, followed by triethylamine (0.74 ml, 5.30 mmol). After stirring overnight at room temperature the solvents were evaporated and the residue suspended in ca. 10 ml methanol. The yellow solid was filtered off, washed with methanol (3×5 ml) and dried in vacuo. Yield: 647 mg (76%) of yellow powder, whose purity was estimated ≥95% by NMR. \(^1\)H NMR (300 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 9.35 (s, 1H, NH), 7.57 (dd, \(^3J = 8.2\) Hz, \(^5J = 1.2\) Hz, 2H\(_{Ar}\)), 7.31 (t, \(^3J = 8.0\) Hz, 2H, 2H\(_{Ar}\)), 7.04 (dt, \(^3J = 7.6\) Hz, \(^5J = 1.2\) Hz, H\(_{Ar}\)), 3.23 (s, 6H, N(CH\(_3\))\(_2\)), 2.31 (s, 6H, CH\(_3\)), 2.25 (s, 6H, CH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (75 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 178.2, 172.4, 149.1, 144.0, 141.2, 128.3 (2C), 128.3, 119.7 (2C), 39.6 (2C), 14.7, 13.8. MS (FAB+): m/z = 399.0396 found, calculated: 399.0404.

2.4.1.5. Complex 10. This compound was prepared analogously to complex 9 from 8 (119 mg, 1.00 mmol), 5 (173 mg, 1.00 mmol), and Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (231 mg, 1.05 mmol); glacial acetic acid and triethylamine were added in corresponding amounts as described above. Yield: 260 mg (77%) of yellow powder, NMR purity ≥95%. \(^1\)H NMR (300 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 7.20 (s, br, 1H, NH), 3.17 (s, 6H, N(CH\(_3\))\(_2\)), 2.81 (s, 3H, NHCH\(_3\)), 2.17 (s, 6H, 2xCH\(_3\)). \(^{13}\)C\(^{1}\)H NMR (100 MHz, dmso-d\(_6\), 25°C, \(\delta\)): 178.0 (2C), 145.0 (2C), 48.9, 29.6 (2C), 14.2, 14.1. MS (FAB+): m/z = 337.6256 found, calculated: 337.6300.

2.4.1.6. Complex 11. The reactants 8 (50 mg, 0.42 mmol) and 7 (151 mg, 0.42 mmol) were stirred in thf (ca. 7 ml) at 50°C for 2 hours. The reaction mixture was cooled down to room temperature and so, and to it Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (92 mg, 0.46 mmol) dissolved in 5 ml methanol was added; After stirring over night at room temperature the solvents were evaporated, the red residue suspended in ca. 5 ml cold methanol, filtered off, washed twice with methanol and dried under vacuum. Yield: 150 mg (68%) of bright red solid, NMR purity ≥95%. \(^1\)H NMR
(300 MHz, dmso-$d_6$, 25°C, δ): 9.47 (s, 1H, NH), 7.60 (d, 3J = 8.0 Hz, 2H, H$_{Ar}$), 7.34 – 7.19 (m, 10H, H$_{Ar}$), 7.08 (t, 3J = 7.8 Hz, 2H, H$_{Ar}$), 6.83 (t, 3J = 7.7 Hz, 2H, H$_{Ar}$), 3.17 (s, 6H, N(CH$_3$)$_2$).

$^{13}$C{$^1$H} NMR (75 MHz, dmso-$d_6$, 25°C, δ): 180.4, 173.7, 150.2, 143.8, 141.4 (2C), 134.8 (2C), 134.0 (2C), 130.8 (2C), 130.5 (2C), 129.1, 128.8 (2C), 128.0 (2C), 127.8, 122.2, 120.6, 39.6 (2C). MS (FAB+): m/z = 522.0586 found, calculated: 522.0600.

Figure 2.4.1. NMR spectra showing that neither demetallation nor decomposition occur when benzimidazole is heated with the Zn(btsc) complex 10.

2.4.2. Stability test. The complex 10 (0.075 mmol, 25.3 mg) was mixed with benzimidazole (4 equiv., 35.44 mg in dmso-$d_6$, and 5 equiv, 44.30 mg in acetonitrile-$d_3$). NMR spectra were recorded immediately at room temperature, and after 18
hours at 75°C. No colour change, precipitation or appearance of the free ligand signals in NMR were observed in these experiments, indicating that no demetallation or other decomposition reactions took place.

2.4.3. Crystallographic Analysis.

2.4.3.1. Crystalisation procedure. The procedure was same for both assemblies. Equimolar amounts of Zn(btsc)9 and ligand (L2 or L3) were weighed in 5 ml Schlenk-tubes equipped with stirring bars, and set under dinitrogen atmosphere. To them ca. 3 ml toluene were added, and the mixture was warmed to 50°C under stirring. Additional toluene was added until everything was fully dissolved. The hot solution was quickly filtered through an HPLC filter into a Pasteur-pipette\textsuperscript{vii} (ca 1.2 ml), in a tall Schlenk-tube, all under dinitrogen. Hexanes were added (ca. 15 ml) into the bottom of the Schlenk-tube (outside of the pipette), which was then tightly closed. It was kept at ambient temperature and protected from light. After two weeks first crystals appeared on inner wall of the pipette (the upper part), which grew to sufficient size in the course of next three weeks.

2.4.3.2. X-Ray Diffraction Analysis. X-ray intensities were measured on a No- nius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda = 0.71073$ Å) at a temperature of 150(2) K. Intensity data were integrated with the Eval14\textsuperscript{152} (assembly 9-L2) or HKL2000\textsuperscript{153} (assembly 9-L3) software. Absorption correction and scaling were performed with SADABS.\textsuperscript{154} The structures were solved with Direct Methods using the programs SHELXS-97\textsuperscript{155} (assembly 9-L2) or SIR-97\textsuperscript{156} (assembly 9-L3). Both structures were refined with SHELXL-97\textsuperscript{155} against $F^2$ of all reflections. Hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.\textsuperscript{157}

Assembly 9-L2. $C_{31}H_{32}N_7PS_2Zn$, MW= 663.10, yellow needle, 0.20 × 0.08 × 0.06 mm$^3$, triclinic, $P$ (no. 2), $a = 11.1142(8)$, $b = 11.1774(9)$, $c = 13.0986(8)$ Å, $\alpha = 81.434(3)$, $\beta = 94.669(4)$, $\gamma = 78.433(2)^\circ$, V = 1573.1(2) Å$^3$, Z = 2, $D_x = 1.400$ g·cm$^{-3}$, $\mu = 1.00$ mm$^{-1}$. 13454 Reflections were measured up to a resolution of $(\sin(\theta/\lambda))_{\text{max}} = 0.50$ Å$^{-1}$. A large anisotropic mosaicity of 1.6° was used for the integration of this weakly diffracting crystal. 3373 Reflections were unique ($R_{int} = 0.056$), of which 2429 were observed ($I > 2\sigma(I)$). 383 Parameters were refined with no restraints. $R1/wR2$ ($I > 2\sigma(I)$) : 0.0867/0.1990. $R1/wR2$ (all refl.): 0.1219/0.2191. $S = 1.071$. Residual electron density between $-0.56$ and 2.23 e·Å$^{-3}$.

Assembly 9-L3. $C_{31}H_{32}N_7PS_2Zn-C_7H_8$, MW= 755.23, orange triangular prism, 0.36 × 0.27 × 0.21 mm$^3$, triclinic, $P$ (no. 2), $a = 12.9582(3)$, $b = 13.0266(2)$, $c = 13.1409(3)$ Å, $\alpha = 115.9892(8)$, $\beta = 93.8687(10)$, $\gamma = 107.0963(9)^\circ$, V = 1855.38(7) Å$^3$, Z = 2, $D_x = 1.352$ g·cm$^{-3}$, $\mu = 0.85$ mm$^{-1}$. 21422 Reflections were measured up to a resolution of $(\sin(\theta/\lambda))_{\text{max}} = 0.57$ Å$^{-1}$. 5715 Reflections were unique ($R_{int} = 0.045$), of which 4719 were observed ($I > 2\sigma(I)$). 447 Parameters were refined with no restraints. $R1/wR2$ ($I > 2\sigma(I)$) : 0.0616/0.1526. $R1/wR2$ (all refl.): 0.0758/0.1615. $S = 1.037$. Residual electron density between $-0.56$ and 1.18 e·Å$^{-3}$.

\textsuperscript{vii} the pipette was previously sealed at the thin end and set within a Schlenk-tube under inert atmosphere.
2.4.4. UV-Vis Titration. To 2.500 ml 50.0·10⁻⁶ mol·l⁻¹ solution of complex 11 in a quartz cuvette, aliquots (5 µl for first 25 points, 10 µl for all following points) of 2.50·10⁻³ mol·l⁻¹ solution of pyridine were added. After each addition, the solution was shaken, left to equilibrate for 1 minute and a UV-Vis spectrum was recorded. Blueshift of the band at 487 nm and of the valley at 420 nm, as well as appearance of the new absorption band at 343 nm were observed upon addition of pyridine. Absorbance values at 529 nm were taken to create plot (A₀ − A) vs c_pyridine, shown in insert in Fig. 2.2.3. The binding constant was calculated using the curve fitting procedure for the 1:1 complexation case, developed by Hunter by having A₀ and K as unknowns, what resulted with A₀ − A_end = 0.0826771 and K=(1.4±0.2)·10⁵ l·mol⁻¹. The fitting using in-house developed curve-fitting scripts gave value of (1.6±0.1)·10⁵, which was more accurate and therefore given in the text.

2.4.5. High-Pressure Infrared Spectroscopy. The autoclave built for the in-situ infrared spectroscopy (in detail described by van Leeuwen et al.), was cleaned, dried, tested for leaks (pressurised with 40 bar hydrogen for 16 hours), and flushed (3×15 bar) with syngas prior to use. All handling and manipulations were performed under oxygen and water-free atmosphere (Ar of 1 bar syngas). Only freshly dried and degassed liquids were used. 1-octene was additionally purified by filtration over a short plug of alumina.

2.4.5.1. HP-IR experiment with the supramolecular ligand. Zn(btsc) complex 9 was weighed (93.85 mg, 235.2 µmol, 14.2 equiv.) on air, transferred into a Schlenk-tube, and repeatedly evacuated and flushed with Ar. 10.0 ml dichloromethane (dcm) and solution of L₄ (20.8 mg, 78.4 µmol, 4.7 equiv.) in 1.0 ml dcm were added to it. The mixture was stirred at room temperature for 30 minutes, and then transferred into the IR-autoclave. The Schlenk-tube was washed with 3.0 ml dcm, which were added to the mixture in the autoclave, which was then again flushed (3×15 bar) with syngas and pressurised to 19 bar. The injection chamber of the autoclave was charged with solution of Rh(acac)(CO)₂ (4.283 mg, 16.6 µmol, 1 equiv.) in 1 ml dcm and pressurised to 30 bar. The autoclave was heated to 40°C (the pressure increased to about 20.5 bar). Background spectrum was taken ca. 1 hour after the temperature reached 40°C, and then the solution of rhodium precursor was injected. The injection chamber was cleaned, dried, charged with 1.0 ml 1-octene solution (521 µl, 3.32 mmol, 200 equiv.) and pressurised again with ca. 30 bar syngas. The incubation was followed all the while. The frequencies around 2000 cm⁻¹ stopped changing ca. 45 minutes after rhodium precursor injection. Four bands (2071, 2056, 2005 and 1970 cm⁻¹) were observed, indicating mixture of two (eq-eq and eq-ap, see main text) rhodium hydride species. In the region of the CO-bridged Rh-dimers no signal appears initially, however, small signals start appearing about two hours after the completed incubation, indicating slow transformation of the hydride species into the inactive rhodium dimeric species. Therefore, in separate experiment the substrate was injected 60 minutes after Rh(acac)(CO)₂ was added, and the reaction monitored. The band of the aldehyde-CO at 1722 cm⁻¹ started growing immediately, and the band of the C=C bond (1639 cm⁻¹) diminished. During the catalysis (18 hours) a weak shoulder at 1986 cm⁻¹ could be observed, possibly the vibration of the the CO-bridged dirhodium species, whose corresponding signal at ca. 1790 cm⁻¹ was observed before the aldehyde band covered it. The signal of the dinuclear rhodium species stayed constant at low intensity.
all the time during catalysis, suggesting that it was in the equilibrium with the catalytically active rhodium species.

2.4.5.2. HP-IR using triphenylphosphine as ligand. This experiment was performed analogously to the previously described one. No Zn complex was added. The amounts of ligand and rhodium precursor used: triphenylphosphine 25 mg (95.3 µmol, 5 equiv.), Rh(acac)(CO)$_2$ 4.920 mg (19.10 µmol, 1 equiv.). The substrate was, however, not added, only the formation of the hydride species was monitored. Like in the above case, four main bands were observed, however at lower frequencies (2056, 2030, 1989 and 1941 cm$^{-1}$). In addition to them, the signals of the dinuclear rhodium species start appearing soon after rhodium injection and are present in significant amount (we estimate about 30% of all rhodium is in form of dimers, based on the relative intensities of the bands in IR).

2.4.6. Catalysis. The Zn(btsc) complexes were weighed directly into the glass inlays before the autoclaves were assembled. After closing, the autoclaves were charged respectively with solutions of the ligand(s), Rh(acac)(CO)$_2$, and the substrate (for the exact amounts amounts see Tab. 2.4.1). Toluene was added at the end to fill the total reaction volume to 5 ml. The charged autoclave was flushed three times with 30–35 bar syngas (CO/H$_2$ = 1 : 1), pressurized to 20 bar and lowered into the previously warmed (40$^\circ$C) oil bath. After 16 or 24 hours, the pressure was released, autoclave cooled, rinsed with nitrogen and the reaction quenched with tributylphosphite (0.5 ml in each reactor). The crude reaction mixture was diluted with dcm (2 –3 drops of reaction mixture per GC vial) and injected into the GC.

Table 2.4.1. Concentrations and amounts of compounds used in catalytic experiments.

<table>
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<tr>
<th>Compound</th>
<th>equiv.</th>
<th>c/(10$^{-3}$mol liter$^{-1}$)</th>
<th>m/mg, or V</th>
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<td>0.903</td>
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<td>550 µl</td>
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<tr>
<td>2- or 3-octene</td>
<td>500</td>
<td>350</td>
<td>275 µl</td>
</tr>
<tr>
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<td>6.98 (20.9)</td>
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<td>5 (15)</td>
<td>3.50 (10.5)</td>
<td>9.80 (29.4)</td>
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