The role of METAMORPhos ligands in transition metal complex formation and catalysis

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Chapter 1

Bifunctional Properties of METAMORPhos ligands in Homogeneous Catalysis

1.1 Introduction

Catalysts are applied in the majority of chemical processes that provide us in our daily needs for food, energy, medicine, etc. With the ever increasing demand for those needs the role of catalysis is becoming more important. Chemists in both industry and academia are challenged to develop catalysts that are faster, more selective, cheaper, safer, robust and environmentally benign, not only to improve existing catalytic processes but also to develop completely new ones.[1] In the field of homogeneous transition metal catalysis this is generally approached by varying the ligands that are coordinated to the applied metal to steer activity and selectivity. Traditionally, ligands functioned merely as spectators and affected the reactivity of a metal center via their electronic donating/accepting abilities and steric properties. However, the role of ligands can be broadened and they can be designed such that they are actively involved during catalysis via for instance hydrogen bonding interactions, redox non-innocence or proton responsiveness (termed bifunctional ligands*). Such features are also found in natural catalysts (enzymes), enabling them to perform rapid and selective chemical transformations.[2]

Substantial effort is still devoted to the development of novel ligands in general and in particular bifunctional ligands, in order to steer catalyst properties and reactivities towards new directions. METAMORPhos ligands were recently developed in our group as a new type of bifunctional ligand based on a sulfonamide-phosphine framework. This chapter will introduce their properties and versatile coordination chemistry in (paragraph 1.2). Their catalytic application in rhodium catalyzed asymmetric hydrogenation and [2+2+2] cyclo-additions will be discussed in paragraph 1.3. Paragraph 1.4 will discuss hydrogen bonding interactions in catalysis on the basis of some illustrative examples from literature as well as

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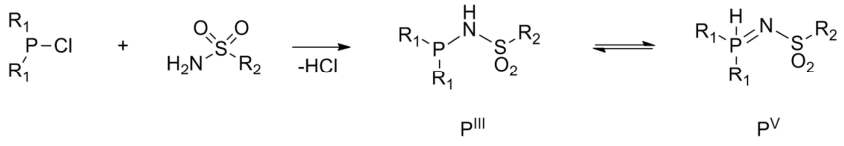
** The terms bifunctional ligand and cooperative ligand are often used in literature describing similar features of a catalytic system, namely the direct involvement of a ligand in a catalytic cycle. Both terms are slightly inadequate descriptions and therefore no clear distinction is found in literature. Bifunctional is a general term directed to describe dual functionalities of a ligands. Dual functionalities do not necessary point towards a synergistic effect of the ligand during catalysis. On the other hand cooperative catalysis is usually defined as a synergistic effect of at least two entities that act together to increase the rate or selectivity of a catalytic reaction. This term is very general and an experimental distinction between cooperative and non-cooperative is difficult to define. At what point is a system/ligand cooperative? Therefore, throughout this manuscript cooperative is used to describe catalytic rate enhancements brought about by the ligand via an additional role next to metal coordination. The term bifunctional is used to describe the functioning of the ligand other than coordination.*

hydrogen bonding interactions found in specific rhodium and iridium METAMORPhos complexes. Paragraph 1.5 will present examples of proton responsive ligands in catalysis and the heterolytic cleavage of H_2 by a METAMORPhos-ruthenium complex. Bimetallic complexes in catalysis will be introduced in paragraph 1.6 as well as a Rh_2(METAMORPhos$_4$) complex which functions in the cooperative asymmetric hydrogenation of alkenes. Imino-bisphosphines (PPN) prepared from METAMORPhos will be described in paragraph 1.7 and paragraph 1.8 will present the aim and outline of this manuscript.

1.2 METAMORPhos ligands

METAMORPhos ligands were first developed by Reek et al. and designed with a hydrogen bonding motif directly connected to a phosphorus atom.[3] These sulfonamide-phosphine ligands, that consist of a completely inorganic backbone (–PNSO$_2$-), can be obtained via a condensation reaction between a sulfonamide and a chlorophoshine or chlorophosphite see Figure 1. A large number of these building blocks are commercially available, enabling the convenient generation of a diverse set of ligands with different electronic and steric parameters. Their name, METAMORPhos, stems from the Greek words *meta*: change and *morp*: shape, because of their ability to adopt different tautomeric forms. They can reside in their P^{III} (PN*H*SO$_2$) or in their P^{V} (P*H*NSO$_2$) oxidation states, which are in equilibrium in solution, see Figure 1. An advantage of this tautomeric equilibrium is the increased stability towards P-oxidation and P-N hydrolysis, as a result of the P^{V} oxidation state. The two tautomeric forms can be readily distinguished by ^{31}P NMR as the P^{V} tautomers have very distinctive H-P coupling constants of around 400-500 Hz. The P^{III}/P^{V} ratios depend on the electron-donating/withdrawing nature of R_1 and R_2. Electron-withdrawing groups on the sulfonamide (R_2) increase the acidity of the NH, which pushes the equilibrium towards the P^{V} tautomer. Reversely, if more electron-donating groups are installed on phosphorus (R_1) its basicity is increased and the equilibrium is also pushed towards the P^{V} tautomer.[4]



Scheme 1. Preparation of METAMORPhos ligands via condensation reaction of a chlorophosphine or chlorophosphite and a sulfonamide and the two tautomeric forms (P^{III} and P^{V}) of the ligand.

To be able to apply these ligands in asymmetric catalysis, chiral versions were prepared. The first chiral METAMORPhos variants (**1**) were obtained via the condensation of binaphthol-PCl and a sulfonamide of choice see Figure 1a.[3, 5] These ligands were isolated as $(HNEt_3)^+(P^{III}NSO_2)^-$ ion pairs (NEt_3 is used as base in the preparation of the ligand) as deduced from X-ray diffraction and ^1H NMR spectroscopic data. Alternatively to BINOL-METAMORPhos ligand **1**, where the chirality is situated in the backbone of the substituents on the phosphorus, several P-chiral METAMORPhos ligands were developed in our group and independently by Verdaguer et al.[6] Reek et al. prepared a P-chiral METAMORPhos, via the condensation of racemic phenyl-anisole-PCl with 4-butylbenzenesulfonamide. The obtained ligand could be resolved (99% ee) using chiral preparative HPLC. Verdaguer et al. prepared P-chiral METAMORPhos **2** from the condensation of various sulfonylchlorides and a P-stereogenic methyl-*tert*-butyl-aminophosphine with the addition of NaH, see Figure 1b. It should be noted that this method differs from our previously described route and offers an alternative strategy for the preparation of METAMORPhos ligands. These P-chiral ligands were applied by Reek et al. in asymmetric hydrogenation of alkenes and by Verdaguer et al. in [2+2+2] cycloadditions, see paragraph 1.3.

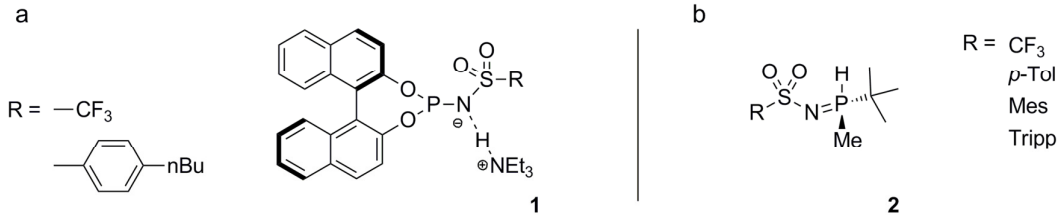


Figure 1. a) Chiral METAMORPhos ligands prepared by Reek et al.[3, 5] b) P-chiral METAMORPhos ligands prepared by Verdaguer et al.[6a] Mes=2,4,6-trimethylphenyl, Tripp=2,4,6-tris(isopropyl)phenyl.

The inorganic $PNSO_2$ framework of METAMORPhos ligands offers a diverse set of coordination modes toward transition metals. Binding can occur via the phosphorus, nitrogen or the oxygen atom of the ligand or via a combination thereof. Besides acting as a neutral ligand scaffold, METAMORPhos ligands contain an acidic NH group that can be deprotonated, leading to an anionic framework. Binding modes ranging from neutral P- and PO-coordination (L and LL'), to anionic (deprotonated) PO^-- and bridged PN^--coordination (LX and μ_2-LX) have been observed with Ru, Rh, Ir, Ni and Pd see Figure 2.

Anionic bonding of METAMORPhos is particularly interesting as this opens up routes for bifunctional bond activation. This has been observed in the heterolytic splitting of hydrogen with a PO^--ruthenium complex wherein the ligand was shown to play a proton responsive role. This will be further discussed in paragraph 1.5. Another interesting aspect of METAMORPhos ligands is their tendency to form PN^- bridged bimetallic complexes. This type of complexes were applied in rhodium catalyzed asymmetric hydrogenation where a

cooperative role of the second rhodium was proven to be essential, this will be further discussed in paragraph 1.6.

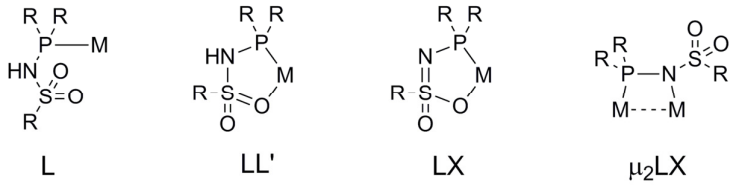
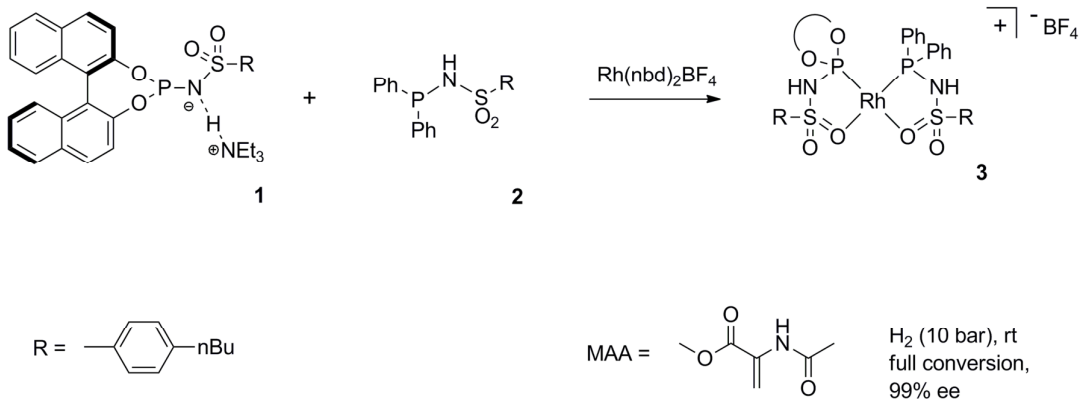


Figure 2. Different bonding modes P, PO, PO^-- and PN^-, observed with METAMORPhos ligands upon coordination to Ru, Rh, Ir, Ni and Pd.

1.3 METAMORPhos in catalysis

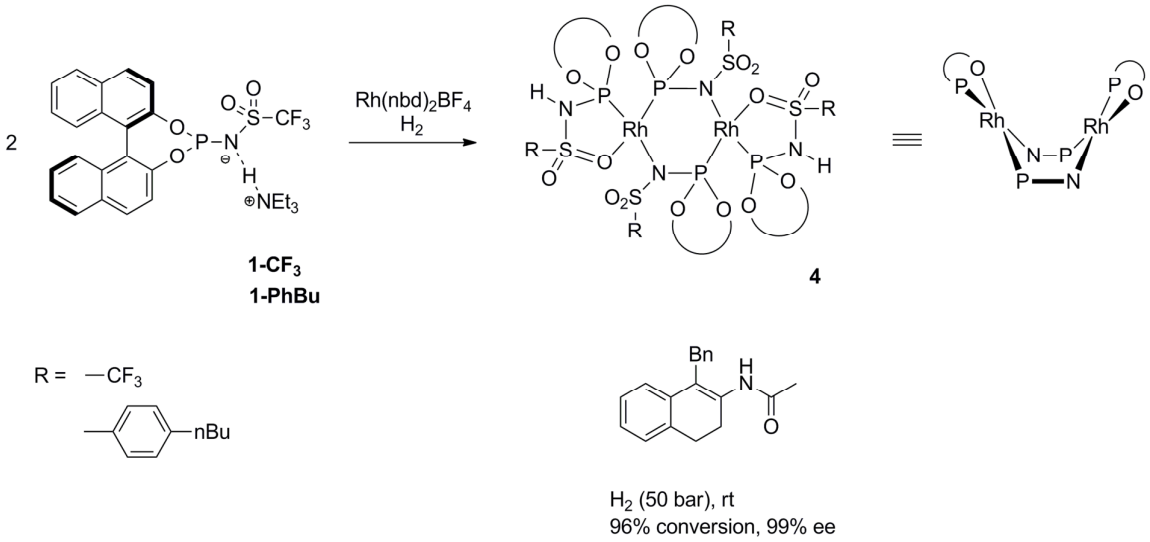
Rh-METAMORPhos complexes were shown to be excellent catalysts for the (asymmetric) hydrogenation of alkenes. The combination of one equivalent **1** and **2** with $[Rh(nbd)_2]BF_4$ selectively generated heterocomplex **3**, see Scheme 2. This cationic complex was shown to be an excellent catalyst for the hydrogenation of methyl-2-acetamidoacrylate (MAA), giving full conversion and high enantioselectivity (up to 99%).[3]



Scheme 2. The combination of one equivalent of **1** and **2** with $[Rh(nbd)_2]BF_4$ leads to the selective formation of heterocomplex **3**, an excellent catalyst for asymmetric hydrogenation of MAA.[3]

In contrast to the formation of mononuclear rhodium complex **3**, reaction of two equivalents of **1** (R = CF_3 or n-BuPh) with $[Rh(nbd)_2]BF_4$ in the presence of H_2 leads to the formation of neutral dinuclear species **4**. These dinuclear species have a boat-shaped geometry with two

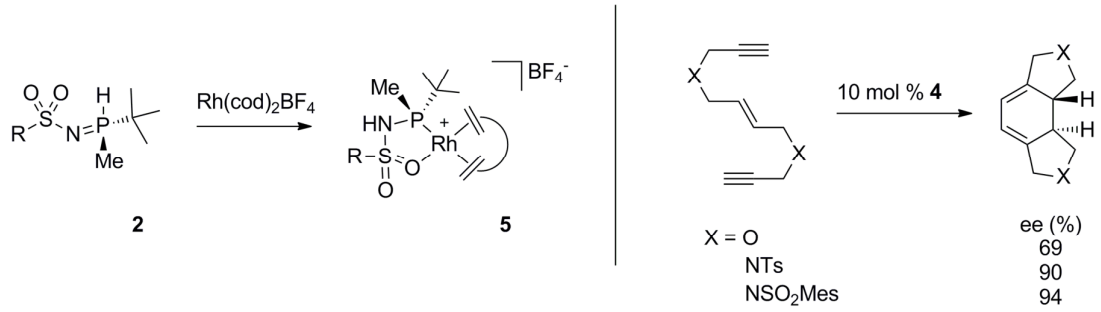
bridging anionic PN^- (μ^2-LX) ligands and two neutral PO-coordinated (LL') ligands, see Scheme 3. These complexes were successfully employed in the catalytic asymmetric hydrogenation of acetamidoalkenes, exhibiting unprecedented enantioselectivities and outperforming traditional cationic mononuclear rhodium catalysts.[6] They were found to remain dinuclear throughout the whole catalytic cycle and, based on computational modeling, a cooperative mechanism involving both metals was proposed, see paragraph 1.6. Since species **4** contains four chiral ligands, these systems are ideal to study non-linear effects in asymmetric hydrogenation.[7] It was observed that the addition of racemic mixture of **1** to $[Rh(nbd)_2]BF_4$ (two equivalents per rhodium) led to self-sorting behavior, providing exclusively homochiral versions of **4**. The racemate of self-sorted homochiral complexes obtained was found to be very insoluble in contrast to the enantiopure homochiral complexes. This led to high enantioselectivities in asymmetric hydrogenation even if the ligand was present in low enantiopurity (40%).



Scheme 3. BINOL-METAMORPhos ligand **1** forms dinuclear complexes (**4**) upon addition of $[Rh(nbd)_2]BF_4$ under H_2 atmosphere. These complexes were successfully applied in the asymmetric hydrogenation of acetamidoalkenes.[5]

As METAMORPhos ligands have successfully been used in asymmetric hydrogenation and a diverse library of (chiral) METAMORPhos ligands can easily be prepared, these ligands are well-suited for evolutionary screening. Therefore they have been investigated in a high-throughput screening study for the iridium catalyzed hydrogenation of the challenging cyclic imine (2,3,3-trimethyl-3*H*-indole).[8] After screening for three weeks, an optimized catalytic system consisting of one chiral and one achiral METAMORPhos ligand with unprecedented activities (TOF 100 h^{-1}) and selectivities (96% *ee*) for this particular substrate were found.
Besides asymmetric hydrogenation, another application of METAMORPhos in catalysis was described by Verdaguer et al.[6a] Upon coordination of **2** to $[Rh(cod)_2]BF_4$, cationic Rh^I

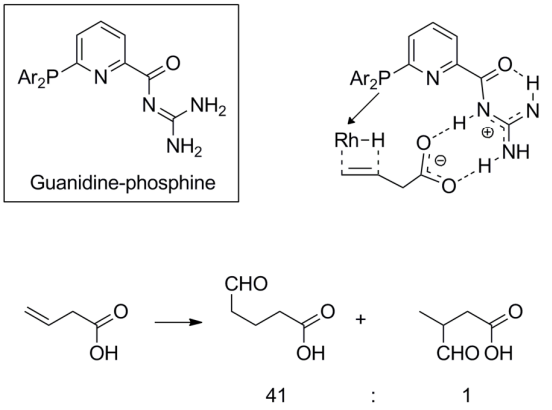
complexes (**5**) were obtained. These complexes were applied in the challenging [2+2+2] cycloaddition of several ene-diynes and high selectivities were obtained (up to 94% ee), see Scheme 4.[6a]



Scheme 4. P-chiral METAMORPhos ligand **2** developed by Verdaguer et al. and the formation of complex **5** with $[Rh(cod)_2]BF_4$. These complexes were applied in the [2+2+2] cycloaddition of several ene-diynes.[6a]

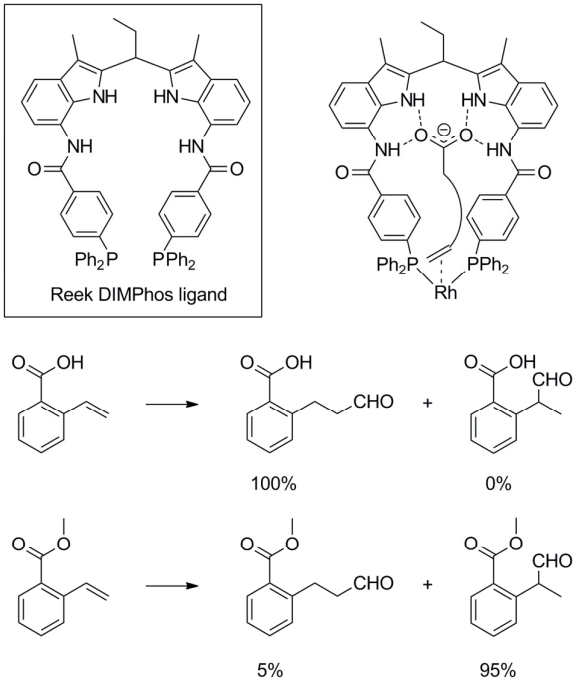
1.4 Hydrogen bonding interactions with bifunctional ligands

Hydrogen bonding interactions between bifunctional ligands and substrates have successfully been applied in homogeneous catalysis. These interactions are used to pre-assemble and pre-activate substrates, thereby lowering the activation barriers of a catalytic transformation. This approach has been successfully applied in the regioselective hydroformylation of unsaturated carboxylic acids by both the groups of Breit and Reek. The former utilized a guanidine-based phosphine ligand coordinated to a Rh^I center. The basic guanidine moiety of this ligand is able to form two hydrogen bond interactions with a carboxylic acid group, enabling strong substrate binding, see Scheme 5. These catalytic systems showed high activity and regioselectivity for the hydroformylation of terminal and internal alkenes.[9] In the hydroformylation of vinylacetic acid the guanidine-based phosphine ligand showed high linear-to-branched ratios (l/b: 41) and an order of magnitude higher activity compared to $Rh(CO)_2(acac)/PPh_3$. Theoretical studies demonstrated that the rate enhancement originates from stabilizing hydrogen bond interactions between the substrate and the ligand (see Scheme 5), lowering transition state energies. This catalytic system has also successfully been applied in decarboxylative hydroformylation and tandem hydroformylation-aldehyde hydrogenation.[10]



Scheme 5. Guanidine-based phosphine ligand applied by Breit et al. in the rhodium catalyzed hydroformylation of unsaturated carboxylic acids.[9]

Reek et al. used a similar approach and achieved unprecedented high regioselectivities with a bidentate DIMPhos ligand, see Scheme 6.[11] It was shown that anionic substrates strongly bind to the DIM-pocket and l/b ratios > 50 were achieved in the hydroformylation of terminal and internal unsaturated carboxylic acids and phosphates. Even more striking, the use of the DIMPhos ligand completely switched the regioselectivity in the hydroformylation of vinylaryls from the branched (α-aldehyde) to the linear product (β-aldehyde), see Scheme 6.

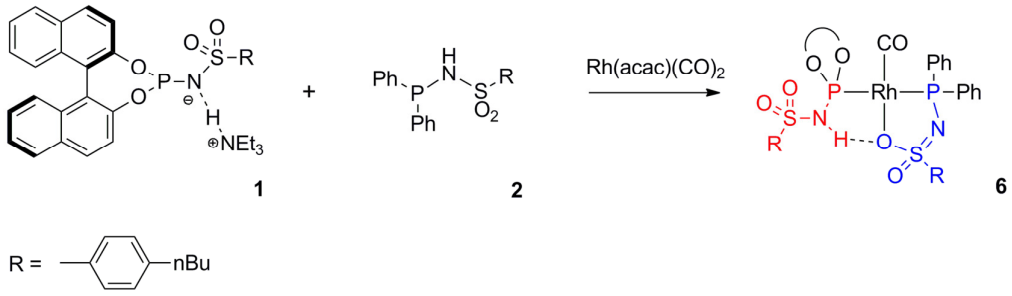


Scheme 6. DIMPhos ligand applied by Reek et al. in the hydroformylation of vinyl arenes, substrates are found to strongly bind in the DIM-pocket leading to high regioselectivities.[11]

In control experiments, in which the hydrogen bond interactions are disrupted by using a methyl ester instead of the carboxylic acid, the linear β-aldehyde is only obtained in minor quantities (5%). Reek et al. has further applied this system in the one-pot isomerization-hydroformylation of terminal olefins towards the production of α-methyl-branched aldehydes and in cofactor-assisted asymmetric hydrogenation of alkenes.[12]

Alternative to ligand-substrate hydrogen bonding interactions, ligand-ligand interactions have been used to generate supramolecular bidentate ligands that were applied in for instance: hydroformylation, asymmetric hydrogenation and alkyne hydration catalysis.[13] These examples illustrate the remarkable activity and selective enhancements that can be achieved using hydrogen bonding ligands. For a more comprehensive overview of hydrogen bonding interactions in homogeneous catalysis see excellent reviews by Dydio et al. and Raynal et al.[14]

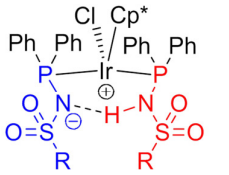
Hydrogen bond interactions have also been found in METAMORPhos-Rh and Ir complexes.[3] Ligand-ligand interactions between neutral and anionic ligands lead to the selective formation of heteroleptic rhodium complexes, see Scheme 7. Coordination of one equivalent **1** and **2** to Rh(acac)$(CO)_2$ led to the selective formation of an unusual *trans*-Rh(**1**, **2**) complex (**6**). The homoleptic complexes Rh(**1**, **1**) or Rh(**2**, **2**) were not observed. In complex **6** one ligand is coordinated in a neutral fashion (**1**, red) while the other (**2**, blue) is deprotonated by $acac^-$ and coordinates in an anionic fashion. *Trans*-P,P-coordination positions the anionic oxygen in an ideal position for hydrogen bond formation with the NH of the neutral P-coordinated ligand. The selectivity for the formation of the heterocomplex originates from the formation of an intramolecular N-H···O hydrogen bond between the neutral and anionically bound ligands, in contrast to typical *cis*-bisphosphine-acac formation.



Scheme 7. Coordination of one equivalent **1** and **2** to Rh(acac)$(CO)_2$ lead to the selective formation of hetero-complex **6** wherein one ligand is neutrally bound (red) and one is anionically bound (blue).

A similar intramolecular ligand-ligand interaction was observed in a Ir(**2**)$_2$Cp*Cl complex (**7**) (unpublished results), see Figure 3. In **7** one ligand is P-coordinated in a neutral fashion, while the second ligand is P-coordinated with an anionic charge localized on the nitrogen, as can be observed from S-N and S-O bond lengths in the crystal structure. A stabilizing hydrogen bond interaction was found between the NH of the neutral ligand and N^- of the

anionic ligand (N···H-N). For related chemistry of METAMORPhos IrCp* complexes see Chapter 6.



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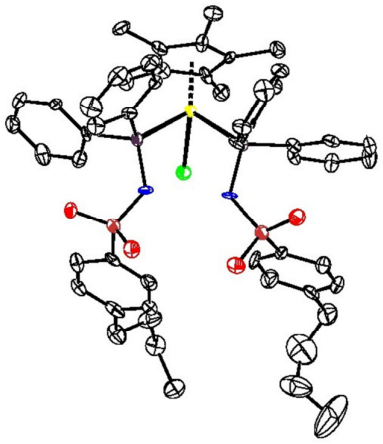
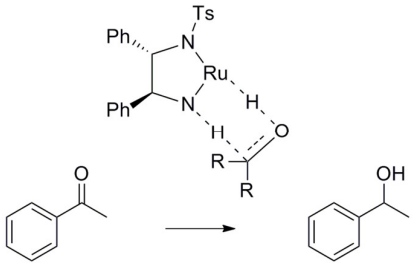


Figure 3. Schematic representation and molecular structure of Ir(**2**)$_2$Cp*Cl complex **7** showing hydrogen bond interaction (N···H-N) between the neutral and anionic METAMORPhos.

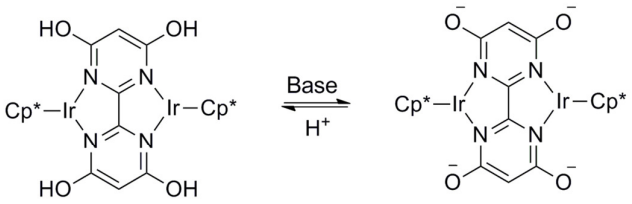
1.5 Proton responsive ligands

Proton responsive ligands are generally defined as ligands that undergo a change in their properties upon gaining or losing a proton.[15] For instance, (de)protonation of a ligand while coordinated to a metal center influences its electron-donating or -accepting abilities and thereby can affect the reactivity of the metal center.[16] This approach is often applied in cooperative catalysis when proton transfer processes are involved. A prominent example of a proton responsive ligand in catalysis is Noyori's amino-ruthenium catalysts for asymmetric (transfer) hydrogenation of ketones and imines.[17] In these highly active systems substrate reduction occurs via a concerted outer-sphere transition state wherein a hydride from the metal and a proton from the ligand transfer simultaneously, see Scheme 8.[18, 19] The active amino-ruthenium hydride species is regenerated via the heterolytic cleavage of H_2 across the formed ruthenium-amido bond (or in the case of transfer hydrogenation, via the H^- and H^+ transfer of a suitable hydrogen donor e.g. isopropanol or formic acid).



Scheme 8. Noyori's ruthenium (transfer) hydrogenation catalyst, applied in the hydrogenation of acetophenone.

Another class of well-known proton responsive ligands are PNP and PNN-pincer ligands that have been employed in several catalytic dehydrogenative coupling reactions by Milstein et al. and in the highly effective hydrogenation of CO_2 by Nozaki et al.[20] In these systems the ligand can also functions as a proton donor/acceptor during catalysis. A different feature of proton responsive ligands was utilized by Fujita et al. who developed a dinuclear Cp*Ir(bipyrimidine) catalyst for the reversible hydrogenation of CO_2 under very mild reaction conditions, a potential system for reversible hydrogen storage.[21] The ligand is equipped with four proton responsive hydroxyl-groups, which could be used to switch the reactivity of the catalyst and act as internal bases during the catalytic cycle. Under basic conditions the hydroxyl groups of the tetrahydroxy-bipyrimidine ligand are deprotonated, which increases the ligands donating ability and activates the catalyst towards CO_2 hydrogenation. By lowering the pH of the solution the hydroxyl groups are reprotonated and the catalyst effectively dehydrogenates formic acid, see Scheme 9.*



HCOOH dehydrogenation catalyst

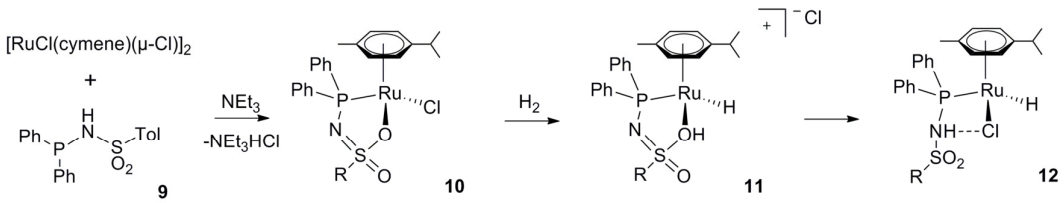
CO_2 hydrogenation catalyst

Scheme 9. Protonated and deprotonated forms of Fujita's dinuclear Cp*Irbipyrimidine catalyst active in the dehydrogenation of formic acid and hydrogenation of CO_2 respectively.[21]

Investigating the proton responsive behavior of METAMORPhos ligands towards ruthenium was particularly interesting since this is the prevailing metal of choice in catalysis involving proton responsive ligands.[22] It was found that upon the addition of **9** to $[RuCl(cymene)(\mu\text{-}Cl)]_2$ (and the addition of NEt_3) piano-stool complex **10** with anionic P,O^--coordination (LX) was obtained, concomitant with the precipitation of triethylammonium chloride,

**It should be noted that proton responsive ligands, next to functioning as an internal acid/base, all have the intrinsic property of being hydrogen bond donor/acceptors, since in essence a hydrogen bond is an incomplete proton transfer. One should therefore consider, when using proton responsive ligands, the possibility of hydrogen bond interactions to play a role during catalytic transformations. Mechanistic investigations of the previously described catalytic systems show that hydrogen bonding interactions were also found to play a role. In theoretical and experimental studies of Noyori's, Fujita's and Nozaki's hydrogenation catalysts, hydrogen bond interactions were found to be involved in lowering activation barriers of the catalytic cycle.[23]*

see Scheme 10. Complex **10** was investigated in the heterolytic splitting of H_2 aiming for reactivities similar to Noyori's catalyst. Indeed complex **10** was found to heterolytically cleave H_2, leading to reprotonation of the ligand and formation of P-coordinated Ru-hydride complex **12**, see Scheme 10. Presumably H_2 is initially cleaved over the Ru-O bond after de-coordination of the chloride to form **11**, after which proton shuttling from OH to NH occurs and the chloride re-coordinates to form **12**. These findings confirm the potential proton responsive character of these ligands.



Scheme 10. Ruthenium piano-stool METAMORPhos complexes **10** and their cooperative activation of H_2 towards formation of **12**.[4]

1.6 Bimetallic complexes

Conventional homogeneous catalysts typically consist of a single metal. In contrast many active sites of enzymes often consist of several (different) metals.[24] The design of homogeneous catalysts containing multiple metal sites has attracted much attention in recent years with the prospect of uncovering new reaction pathways.[25] Next to their potential for new reactivity, homo- and hetero-multimetallic complexes have shown improved activities compared to monometallic systems for a number of reaction types. One of the first examples of bimetallic cooperative catalysis was reported by Stanley et al. that used a dicationic Rh^{II}-Rh^{II} complex in the hydroformylation of terminal alkenes.[26] This bimetallic catalyst showed high catalytic activity compared to its monometallic systems. The reductive elimination of the aldehyde is often believed to be the rate-determining in these monometallic systems.[28] This potential rate-determining step is circumvented by this dicationic Rh^{II}-Rh^{II} complex via a cooperative intramolecular hydride transfer from one rhodium center to the other, see Figure 4a. Similar hetero-bimetallic complexes containing rhodium and ruthenium were prepared and applied in the catalytic hydroformylation of 1-octene, see Figure 4b.[27] High selectivities towards the linear aldehyde were obtained and a cooperative role of the ruthenium metal was proposed in the form of an intramolecular hydride transfer or in the form of ruthenium acting as a labile ligand. Although selectivities were enhanced, activity of the catalyst was lower than its mononuclear counterpart. For more comprehensive overviews of bimetallic cooperative catalysis see excellent reviews by Hong et al.,[25b] Gomez et al.,[25a] and Reek et al.[28]

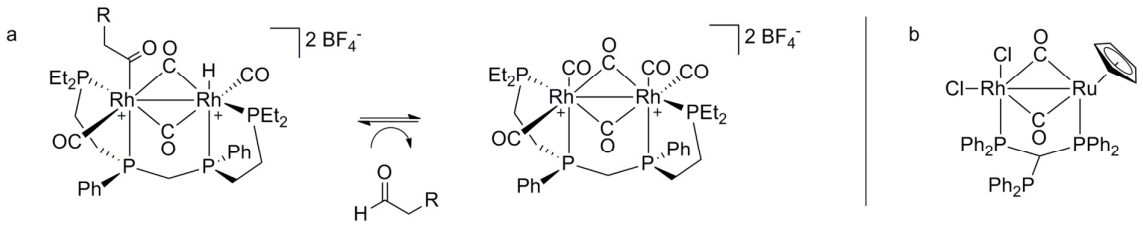


Figure 4. (a) Stanley's dicationic Rh^{II}-Rh^{II} bishydride complex[26] and (b) bimetallic Rh/Ru complex[27] both were applied in catalytic hydroformylation of terminal alkenes.

As already eluded to in paragraph 1.3, METAMORPhos was shown to form neutral dinuclear rhodium complexes (**4**) that were highly active in asymmetric hydrogenation reactions. A cooperative mechanism with involvement of both metals was proposed to be operative for hydrogenation with complex **4**, based on DFT calculations and in situ NMR spectroscopy, see Figure 5. These dinuclear complexes adopt a boat-like conformation (**A**) and the calculated Rh-Rh distance (3.23 Å, which is in agreement with Rh-Rh distance found in the X-ray structure 3.2276(7) Å) is in the range of a (weak) Rh-Rh bond. It turned out that (cooperative) H_2 activation over both rhodium centers is energetically favored over heterolytic H_2 splitting over the Rh-N bond or conventional oxidative addition of H_2 to a single rhodium center. This leads to bis-hydride species **C**, via initially formed H_2-adduct species **B**, containing one terminal and one bridging hydride. The formation of a bridged hydride shortens the Rh-Rh distance to 3.16 Å. This hydride is bound more strongly to the Rh-center with the terminal hydride, as suggested by the difference in Rh-H bond lengths (1.65 Å versus 1.84 Å). Therefore **C** is best described as a mixed valent Rh^{III}-Rh^{I} complex. Strikingly, a significant increase in Rh-O bond length *trans* to the Rh^{I} is observed in **C** (from 2.24 Å to 2.94 Å), which is probably due to the strong *trans*-influence of the Rh^{I} center. This generates a vacant coordination site for substrate coordination (ethylene was used as a model substrate) giving species **D**. Migratory insertion of the substrate into the terminal Rh-H bond produces alkyl species **E**, which rearranges to energetically favored species **F**. The alkyl is now *cis* to the bridging hydride and reductive elimination can occur, regenerating complex **A**. This cycle clearly shows the cooperative effect in this bimetallic system that accounts for their unprecedented activity: 1) H_2 is activated over both metals and 2) the *trans*-influence of Rh^{I} induces σ-lability of the neutral P,O coordinated ligand, generating a good binding site for a π-accepting alkene.

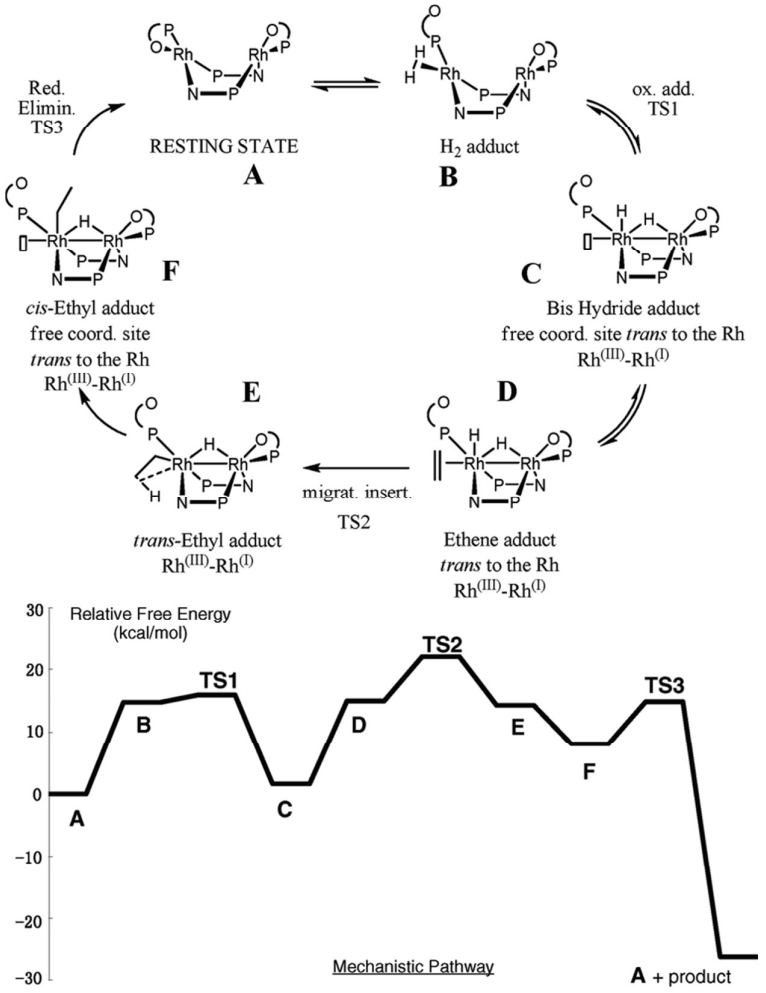
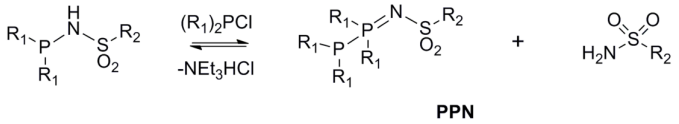


Figure 5. Proposed cooperative hydrogenation mechanism of alkenes with complex **4** based on DFT calculations.

1.7 imino-bisphosphine ligands

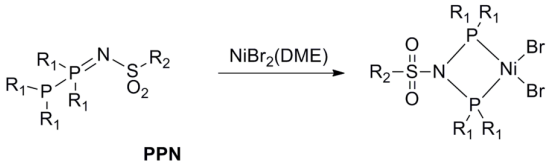
Besides their versatile coordination chemistry, METAMORPhos ligands also display reactivity as free ligand. Next to the described tautomerism, these systems can condense with an additional equivalent of $(R_1)_2PCl$ to form imino-bisphosphines (P-P=N), see Scheme 11. The equilibrium between METAMORPhos and PPN is determined by the R_1 and R_2 substituents. Bulky R_1 groups shift the equilibrium towards the METAMORPhos site while electron-withdrawing R_2 groups shift the equilibrium towards the PPN site. The equilibrium can be pushed towards PPN by the addition of two equivalents of $(R_1)_2PCl$. Isolation of the initially found METAMORPhos followed by subsequent addition of a different chlorophosphine

affords routes to the selective preparation of imino-bisphosphines with two differently substituted P-atoms.



Scheme 11. The equilibrium between METAMORPhos and imino-bisphosphines (PPN).

Interestingly, upon coordination to $NiBr_2$(DME) (DME = 1,2-dimethoxyethane) the imino-bisphosphines rearrange to diphosphinamines (P-N-P) and P,P-chelated nickel complexes were obtained. These complexes were applied in ethylene oligomerisation, see Scheme 12.[29]



Scheme 12. The formation of imino-bisphosphines **PPN** and the rearrangement to a diphosphinamines upon coordination to $NiBr_2$(DME).[29]

1.8 Aim and outline of this manuscript

METAMORPhos ligands are intriguing because of their proton responsive/hydrogen bonding features in combination with their tendency to form bimetallic complexes. First, it would be interesting to study whether these features can be combined and can lead to new type of reactivities. A promising approach to towards combining these features is by creating bisMETAMORPhos ligands. Secondly, expanding their coordination chemistry beyond Rh, Ru to other transition metals that have also shown wide applicability in homogeneous catalysis (e.g. iridium and palladium) might generate additional insight in the chemistry of these ligand systems and their potential applications.

In **Chapter 2** of this manuscript, the preparation of a bisMETAMORPhos ligand is described and its coordination to Ir^{I}(acac)(cod). This ultimately generates an Ir^{III}(hydride) complex that is applied in the base-free dehydrogenation of formic acid. In **Chapter 3**, this work is extended to include a small series of bisMETAMORPhos ligands with different electronic and steric properties. The ligand structure affects the rate of base-free dehydrogenation of formic acid. The bifunctional role of the ligand, in particular its role as internal base and

hydrogen bond acceptor/donor is described. In **Chapter 4**, the same catalytic system is investigated in the hydrogenation of CO_2, by high pressure NMR studies. In **Chapter 5**, the formation of an unconventional bisMETAMORPhos$_2$-Pd^{I}-Pd^{I} dimer is shown and a mechanism for its formation is proposed. This complex was applied in the Suzuki-Miyaura cross coupling of aryl chlorides. **Chapter 6** shows the prepartion of rhodium and iridium piano-stool METAMORPhos complexes and their cooperative activation of H_2 and alkynes and describes the formation of an unconventional four-membered Ir-P-N-C ring via intramolecular C-N bond formation. In **Chapter 7**, the preparation of a -PNSO$_2$NP-bisMETAMORPhos ligand is described and used in the formation of bimetallic iridium/rhodium complexes. A bimetallic iridium complex was found to undergo intra-molecular C-H activation of the ligand, generating a bimetallic complex contain two non-equivalent iridium centers.

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