

Ligand Self-Sorting and Nonlinear Effects in Dinuclear Asymmetric Hydrogenation: Complexity in Catalysis

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Nature has been a source of inspiration for scientists as billion years of evolution have resulted in magnificent examples of how processes can be controlled efficiently. In the field of supramolecular catalysis, enzymes have been the major source of inspiration. As such, many synthetic systems have been prepared to mimic certain aspects of enzymes, with a strong focus on connecting catalytically active sites to cavities or binding sites having affinity for the substrate.^[1,2] Although such approaches have resulted in interesting new tools to control selectivity,^[3–5] we are not nearly close to the abilities of Nature to control chemical transformations. One of the major differences between Nature and synthetic approaches is that in biological systems, chemical processes take place in a complex out-of-equilibrium environment.^[6] In a cell, many chemical transformations occur simultaneously or in controlled sequence, involving an impressive number of different components. An important challenge for biologists is to understand how this organized complexity leads to emerging properties. As a result, new fields such as systems biology^[7] including non-equilibrium thermodynamics^[8] have been developed. Synthetic chemists traditionally aim for systems that are as clean and pure as possible,^[9] and it is only recently that complexity in chemical systems received attention.^[10–12] Despite the interesting perspectives, complexity in homogeneous catalysis has not been a research focus in itself, although many aspects related to complexity have been reported. Product inhibition and catalyst poisoning are relevant to complex chemistry as they imply processes with feedback loops. Dynamic catalyst libraries and combinatorial catalysis require selection procedures,^[6,13] and nonlinear effect (NLE) in asymmetric catalysis^[14–16] can lead to emerging properties. With this in mind we decided to study in detail NLE using dinuclear hydrogenation catalysts **C** that have four chiral ligands. Application of non-

enantiopure ligands can lead to formation of heterochiral complexes (with more than two chiral ligands) with different properties and these complexes can theoretically be more active and selective than their homochiral analogues.^[16] Catalytically active complexes with four chiral ligands are rare, and for hydrogenation complex **C** is, to the best of our knowledge, the only example. The use of a racemic ligand could lead to the formation of ten stereoisomers of **C** (Figure 1).

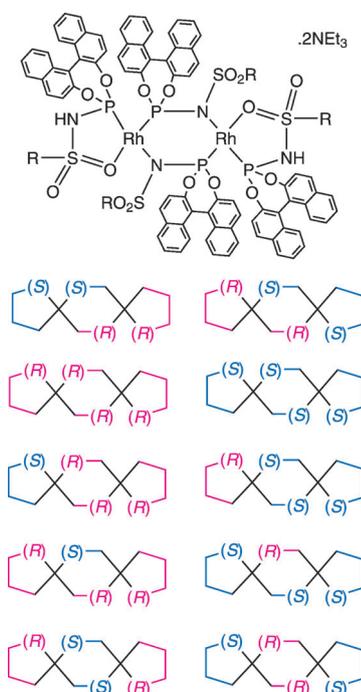


Figure 1. The $[\text{Rh}_2(\text{L})_4]$ complex **C** and a schematic representation of the 10 potential complexes that can form from a racemic mixture (pink represents the ligand in *R* configuration and blue the *S*). For **L1**, $\text{R} = 4\text{-}n\text{-butylbenzene}$, for **L2**, $\text{R} = \text{CF}_3$ and for **L3**, $\text{R} = \text{CH}_3$.

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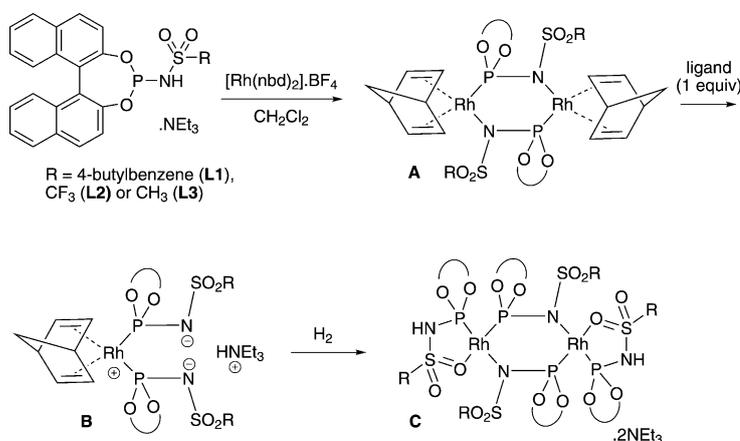
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Herein we report the self-sorting of chiral ligands at these tetraligated complexes, but not for some of the precursor complexes, the in situ enantiopurification of the system caused by the relative insolubility of the racemate of homochiral complexes. As a result, in asymmetric hydrogenation using non-pure ligands ($S/R = 70:30$) the product can be formed in high enantiopurity (90% *ee*). The outcome, however, is strongly dependent on starting conditions (concen-

tration, incubation, substrate) as intermediate complexes towards the formation of **C** are not self-sorted and yet active in hydrogenation.

The METAMORPhos family, a new class of sulfonamide-phosphorus ligand was recently disclosed.^[17–19] Their coordination to rhodium gives rise to unique complexes consisting of two metal centres and four METAMORPhos ligands [Rh_2L_4] (**C**). Two deprotonated ligands form a bridge between the two metals and two ligands coordinate in a P–O chelating fashion. These complexes display unrivalled high selectivity in asymmetric hydrogenation of benchmark substrates and challenging substrates such as cyclic enamides.^[19]

Studies on the coordination chemistry of enantiopure ligands revealed that **C** is formed from the precursor [$\text{Rh}(\text{nbd})_2$] BF_4 (nbd = norbornadiene) in three steps (Scheme 1). One equivalent of ligand (**L1**, **L2** or **L3**) reacts with the met-



Scheme 1. Coordination of the METAMORPhos ligands to rhodium in three steps to form the final tetraligated dinuclear complex **C**.

allic precursor to yield **A**, [$\text{Rh}_2\text{L}_2(\text{nbd})_2$], a bimetallic complex where two METAMORPhos ligands form a bridge between the metals, and each rhodium atom is chelated by an nbd ligand. This dimeric complex reacts with two additional ligands (one per rhodium atom) to give the monomeric complex **B**, [$\text{RhL}_2(\text{nbd})$]. The monomeric nature of this complex is evident from the mass spectrum and the doublet in the ^{31}P NMR spectrum, indicating a symmetric complex with one rhodium atom and two ligands. The structure of this complex is similar to the precatalyst synthesized from monodentate phosphorus ligands, such as the well-studied MONOPhos.^[20] The final dimeric complex [Rh_2L_4] quantitatively forms when 5 bars of H_2 is applied to this monomer, which effectively removes the nbd ligands.

We explored the coordination of racemic ligands under the same conditions for the formation of the three complexes **A–C**. When a racemic mixture of ligand is used, three diastereomers of **A** can be formed: [$\text{Rh}_2((R)\text{-L})_2(\text{nbd})_2$], [$\text{Rh}_2((S)\text{-L})_2(\text{nbd})_2$] and [$\text{Rh}_2((R)\text{-L})((S)\text{-L})(\text{nbd})_2$]. Surprisingly, the ^{31}P NMR spectrum of **A** is identical for complexes based on (*R*)-**L1** and (*rac*)-**L1**, suggesting that

only homocomplexes [$\text{Rh}_2((R)\text{-L})_2(\text{nbd})_2$] and [$\text{Rh}_2((S)\text{-L})_2(\text{nbd})_2$] are formed as the diastereoisomer is expected to give a different signal in the NMR spectrum. To confirm this self-sorting behaviour, the experiment was repeated using pseudoenantiomers (*S*)-**L1** and (*R*)-**L2**, mirror-image ligands that have a different R group on the sulphonamide. In this experiment also, only homochiral complexes [$\text{Rh}_2((S)\text{-L1})_2(\text{nbd})_2$] and [$\text{Rh}_2((R)\text{-L2})_2(\text{nbd})_2$] can be seen in the ^{31}P NMR spectra (Figure 2). Control experiments show that the substituents on the sulphur atom are not responsible for this chiral self-recognition.^[19,21]

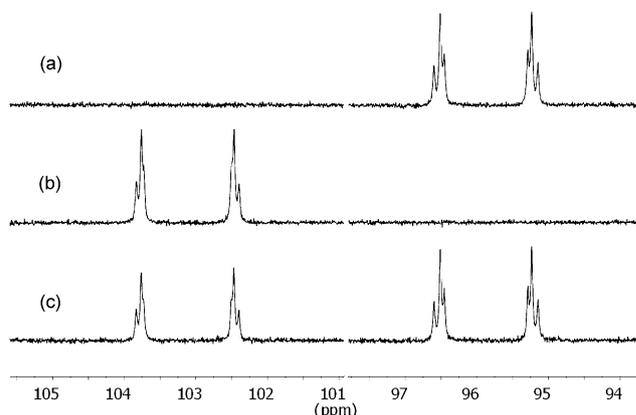


Figure 2. ^{31}P NMR spectrum of [$\text{Rh}_2\text{L}_2(\text{nbd})_2$] synthesized from a) (*S*)-**L1**, b) (*R*)-**L2** and c) a mixture of (*S*)-**L1** and (*R*)-**L2**.

The reaction of [$\text{Rh}(\text{nbd})_2$] BF_4 and (*rac*)-**L2** also resulted in the formation of self-sorted homochiral complexes, as showed by the ^{31}P NMR spectrum (see the Supporting Information) and further confirmed by X-ray analysis (Figure 3). The homocomplexes **A**, [$\text{Rh}_2((R)\text{-L2})_2(\text{nbd})_2$] and [$\text{Rh}_2((S)\text{-L2})_2(\text{nbd})_2$], crystallize as a racemate of homochiral complexes. Notably, the ligands have the same coordination mode and the complex has the same conformation as previously established by NMR studies and DFT calculation.^[19]

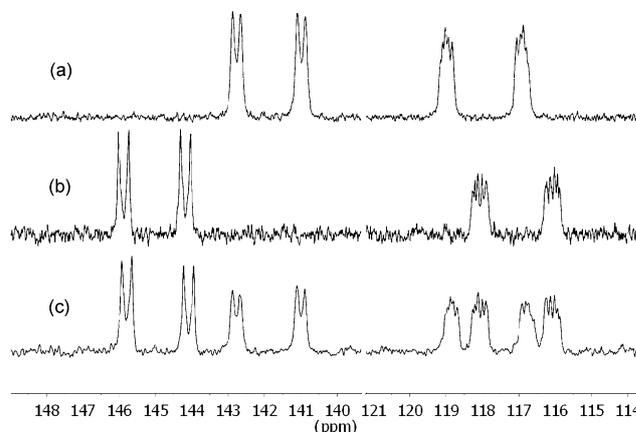


Figure 3. ^{31}P NMR spectrum of [Rh_2L_4] synthesized from a) (*R*)-**L2**, b) (*S*)-**L3** and c) a mixture of (*R*)-**L2** and (*S*)-**L3**.

In contrast to what is observed for complex **A**, if (*rac*)-**L1** (or (*rac*)-**L2**) is used to form complex **B**, the ³¹P NMR spectrum shows two doublets in a 1:1 ratio indicating the formation of two diastereomeric complexes. One of the doublets corresponds to the previously observed homochiral complex [Rh(**L**)₂(nbd)], whereas the other indicates the formation of a *meso* heterochiral complex. X-ray diffraction confirmed the monomeric nature of the complex. Just as observed for complex **A**, **B** crystallizes as a racemate of homochiral complexes (crystals of the heterochiral complex were not obtained).

When two equivalents of (*rac*)-**L1** were reacted with [Rh(nbd)₂]BF₄ under H₂ pressure to form complex **C**, the ³¹P NMR spectrum of the solution was identical to the very characteristic AA'BB'XX' pattern observed for the homochiral complex **C** prepared from (*R*)-**L1** (see the Supporting Information). This suggests that **C** forms with a high fidelity chiral self-sorting: only [Rh₂((*R*)-**L1**)₄] and [Rh₂((*S*)-**L1**)₄] are present in solution. To confirm these findings, we used pseudoenantiomers consisting of (*S*)-**L1** and (*R*)-**L2**. This strategy allowed us to distinguish the pseudodiastereomers by mass spectroscopy and gave a better separation of the ³¹P NMR signals. Mostly homochiral complexes were formed, but now the self-sorting was not perfect: minor side products could be distinguished by spectroscopic techniques (see the Supporting Information). Control experiments show that the substituent on the sulphur atom is not responsible for self-sorting. Using a mixture of (*S*)-**L1** and (*S*)-**L2** to form complex **C** leads to a multitude of signals in ³¹P NMR consistent with a statistical mixture of complexes (see the Supporting Information). The use of the structurally more similar ligands (*R*)-**L2** and (*S*)-**L3** showed strong self-sorting behaviour, as only homochiral complexes could be seen in the ³¹P NMR spectrum (Figure 3). In line with this, in the MS spectra, only homocomplexes could be identified.

The reaction of two equivalents of (*rac*)-**L2** with [Rh(nbd)₂]BF₄ under H₂ pressure yielded a compound that is very poorly soluble in dichloromethane. Analysis by NMR spectroscopy was prohibited by the low solubility, but X-ray structure determinations on isolated crystals demonstrated that the solid state consisted of the racemate of the homochiral complexes **C** (see Figure 4). Like for complex **A**, these crystal structures confirmed the coordination mode of the ligands, previously established by NMR studies, as well

as the boat-shaped conformation, previously proposed on the basis of DFT calculations. A noticeable difference between the calculated and the crystallized complex is that the P–O coordinated ligands are deprotonated by triethylamine in the solid state.

Before evaluating nonlinear effects in the hydrogenation of the benchmark substrates dimethylitaconate (**4**) and methyl-2-acetamidoacrylate (**5**), we first determined the solubility of the racemate of homochiral complexes based on ligand **L2** in pure dichloromethane and in the presence of typical amounts of the substrates (substrate/Rh ratio of 25 and initial Rh concentration of 25 mM), as this plays a role in the anticipated nonlinear effects. In the absence of substrate, the solubility of the racemic self-sorted complex is 0.64 mM. Interestingly, the presence of substrate **4** reduces this solubility to 0.41 mM whereas **5** increases it to 1.58 mM, substrate-induced properties that could influence the catalytic outcome of the reaction. We first hydrogenated **4** using complexes based on ligands **L2** with an enantiopurity of the ligand varying between 0 and 100%. At high catalyst concentration ([Rh]=25 mM), when the complexes are preformed prior to substrate addition, precipitation of the racemate occurs, leaving in solution homochiral complexes of the ligand that is in excess. Subsequent addition of substrate **4** enhances this enantiopurification of the reaction mixture by lowering the solubility of the racemate even further. This explicit reservoir effect^[14,16] leads to a very strong positive nonlinear effect. Lowering of the enantiomeric excess of the ligand from 100 to 40%, leads to a drop of only 7% for the *ee* value of the product (Figure 5). Importantly, the same experiments but without incubation that allow this self-sorting process and precipitation to occur, results in the opposite effect. Instead of a positive nonlinear effect, a strong negative nonlinear effect is observed. This suggests that under these conditions, catalysis happens before self-sorting and subsequent precipitation has completed. The kinetic complexes formed before the metal–ligand system reaches a thermodynamic equilibrium are responsible for most of the conversion.

Similar hydrogenation experiments of **4** were done under more diluted conditions ([Rh]=2 mM), again with and without complex preformation prior to substrate addition. The same results are obtained in both these experiments, as expected, as under these dilute conditions no precipitation

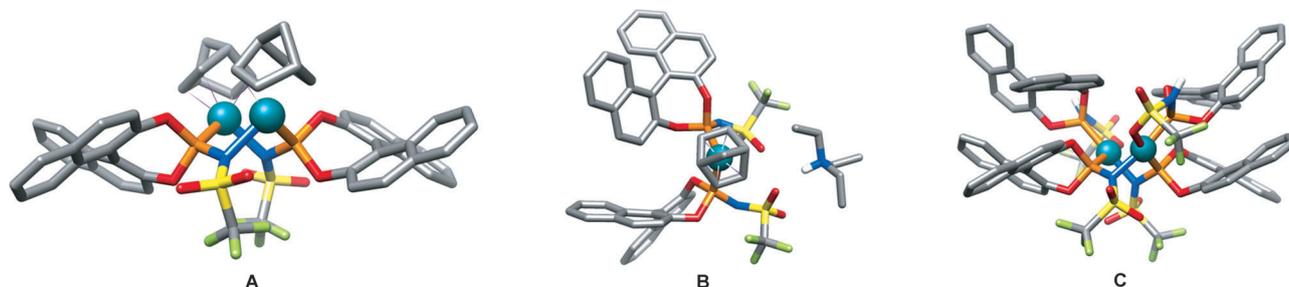


Figure 4. Crystal structures of **A**, **B** and **C** synthesized from (*rac*)-**L2**. Hydrogen atoms, solvent and, in the case of **C**, the triethylammonium counterion are omitted for clarity (see ref. [22]).

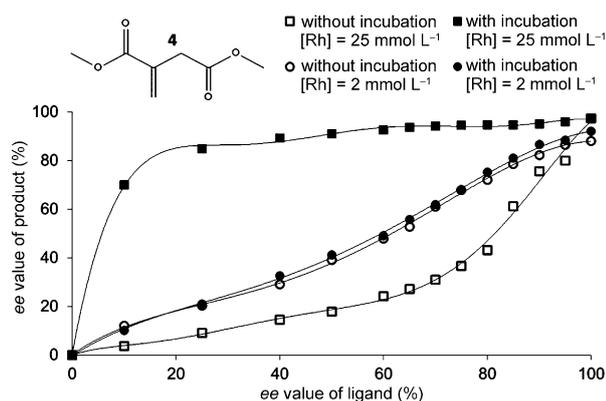


Figure 5. NLE curves for the hydrogenation of **4** with **2** as a ligand.

spontaneously occurs after incubation. The small deviation from linearity for the curve of *ee* value of product as a function of *ee* value of ligand may be due to imperfect self-sorting (as also observed the NMR experiment using (*S*)-**L1** and (*R*)-**L2**). We attempted to record the ³¹P NMR spectrum of the reaction mixture (with a racemic ligand) under these catalysis conditions to see these heterocomplexes arising from incomplete self-sorting. Unfortunately, even after an overnight acquisition, the signal-to-noise ratio was too small and only the signals for the homochiral complexes could be observed. In the NMR tube, crystals of the self-sorted racemate had appeared during the NMR experiment, (their nature was confirmed by X-ray crystal structure determination). Apparently, the amount of non-self-sorted complexes is very small, yet they have an influence on the outcome of the reaction.

Similar studies on the nonlinear behaviour of the complexes were performed using substrate **5**. For [Rh]=25 mM, the results were comparable as those observed for **4**. However, the nonlinear effect observed after incubation is less pronounced (Figure 6), likely owing to the substrate-induced higher solubility of the racemate of self-sorted complexes. This shows that a feedback loop operates, in which the substrate controls, by solubility of complexes, the outcome of its own hydrogenation. For [Rh]=2 mM, the results with and

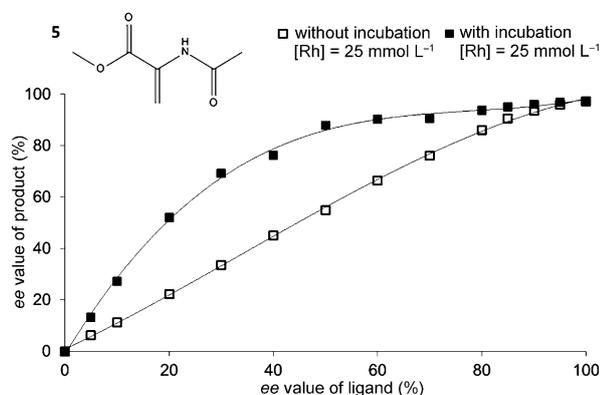


Figure 6. NLE curves for the hydrogenation of **5** with **2** as a ligand.

without complex preformation were significantly different, showing that for this substrate, hydrogenation is significantly faster than the formation of the self-sorted complexes (see the Supporting Information). Like observed for the hydrogenation of **4** (at [Rh]=25 mM), the kinetically formed active complexes give different selectivity than the thermodynamic self-sorted complexes. The exact nature of those complexes remains elusive, as they convert very fast into the stable dimer and no direct observation could be made. In analogy with well-known systems, we expect solvated bis-ligated monomers to be active intermediates.^[20] As they are formed from the non-self-sorted intermediate **B**, they are not self-sorted either, and the weakly coordinated solvent molecules make them very reactive towards H₂ and substrates.

In summary, we studied in detail a catalytic system for asymmetric hydrogenation based on METAMORPhos ligands and rhodium as a complex chemical system. These studies revealed self-sorting of ligands at dinuclear complexes leading to homochiral complexes, behaviour that is not observed for the mononuclear complexes that form during the incubation phase of a hydrogenation experiment. We confirmed the nature of dimeric and mononuclear complexes with their X-ray structure. The racemate of the self-sorted homochiral complex [Rh₂(**L2**)₄] synthesized from the racemic ligand were found to be very insoluble. This property leads to a very strong positive nonlinear effect in asymmetric hydrogenation, with a high *ee* value obtained for the product while the ligand is present in low enantiopurity (40%). This is, however, only observed when the substrate is introduced after an incubation time in which the self-sorted complexes are formed. Addition of the substrates at the beginning of the experiment gives completely different effects showing that intermediate complexes, which form before the thermodynamic equilibrium of the ligand–metal system is reached, are catalytically active. The complexity of the system was further demonstrated by showing a feedback loop: the substrate influences the solubility of the racemate of homochiral complexes, a characteristic that is important for the nonlinear effects observed. The substrate thus influences the extent of nonlinear effect. This is the first example of self sorted ligation at dinuclear complexes that are active in asymmetric hydrogenation. Detailed information as presented here is relevant for process optimization and development of more complex catalytic systems that may play an important role in future processes.

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Keywords: asymmetric catalysis • complexity • hydrogenation • nonlinear effects • self-sorting

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- [21] Usually, narcissistic self-sorting and self-recognition are used indifferently. In the case of chiral self-sorting, the term “narcissistic” is misleading as Narcissus fell in love with his reflection (his mirror image).
- [22] CCDC-931393 (A [Rh₂(L₂)₂(nbd)₂]), 931394 (B [Rh(L₂)₂(nbd)]), 931395 (C [Rh₂(L₂)₄] recrystallized from nitromethane) and 931396 (C [Rh₂(L₂)₄] recrystallized from dichloromethane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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