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Molecular Insights into the Ligand-Reactant Interactions of Pt Nanoparticles Functionalized with α-Amino Acids as Asymmetric Catalysts for β-Keto Esters

Anda Šulce,[a] Nico Mitschke,[b] Vladimir Azov,[c] Sebastian Kunz*[a]

[a]Institute of Applied and Physical Chemistry (IAPC), Center for Environmental Research and Sustainable Technology, University of Bremen, Leobener Straße 6, 28359 Bremen, Germany

[b]Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, Carl-von-Ossietzky-Straße 9-11, 26111 Oldenburg, Germany

[c]Department of Chemistry, University of the Free State, PO Box 339, Bloemfontein 9300, South Africa

* Corresponding Author:
PD Dr. Sebastian Kunz
University of Bremen
Institute of Applied and Physical Chemistry (IAPC)
D-28359 Bremen
Tel: +49-421-218 63187
eMail: SebKunz@uni-bremen.de

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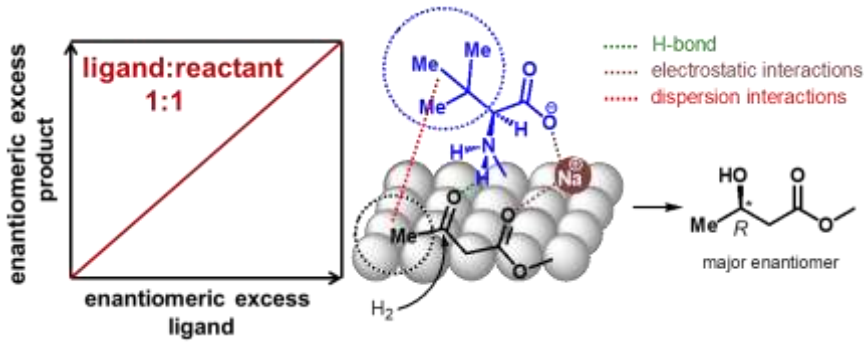

Understanding of ligand-reactant interactions: In the asymmetric hydrogenation of ß-keto esters over α-amino acid-functionalized supported Pt nanoparticles the stereoselectivity is mainly determined by a 1:1 ligand-reactant interaction and further influenced by small geometric changes in the ligand structure as well as by the alkali metal cation coordinated to the ligand.

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Abstract

The asymmetric hydrogenation of ß-keto esters over α-amino acid-functionalized Pt nanoparticles was explored in order to expand our understanding of ligand-reactant interactions underlying the chiral induction. A comprehensive investigation aimed at the quantification of the nonlinear effects demonstrated that for most of the ligands and reactants enantiodifferentiation is determined by 1:1 ligand-reactant interaction. However, attachment of phenyl substituents to the ligands or reactants likely involves the formation of more intricate intermediate complexes. We have shown that the asymmetric bias is sensitive to even small changes in the geometry of the ligand. Additionally, we have found that alkali metal cations, which balance the negative charge of the ligand's carboxyl group and originate from the metal hydroxide used for ligand functionalization, play a key role in the process of chiral induction. As the nature of the cation can be varied by simply changing the metal hydroxide used during functionalization, this finding opens an additional possibility to control the stereoselectivity by tuning the ligand-reactant interaction.

Introduction

Due to the key role of supported precious metal catalysts in multiple industrial processes, the control of selectivity of such catalysts is of fundamental importance for the improvement of resource utilization.[1] Nanoparticles (NPs), which are used for the preparation of supported metal catalysts, exhibit a variety of surface atoms (e.g. corner, edge, and terrace atoms) of different chemical character and activity.[2] Furthermore, groups of adjacent surface atoms can form ensembles capable of distinctive reactivities.[3] This leads to a broad variety of catalytically different sites on the surface of a NP.[4] As all these different sites can transform reactants in different ways, the control of selectivity is generally challenging for nanoparticle-based catalysts and requires strategies to modify the catalytic surface.

The most successful approach to improve selectivities by modification of supported catalysts is the use of bimetallic systems, which led e.g. to the development of lead free gasoline production process.[5] Incorporation of a second metal into a NP causes changes of its electronic structure.[6] This in turn can alter binding energies of reactants as well as of intermediates and, as a result, can lead to improved selectivities.[7] Furthermore, the number, size, and chemical identity of active atomic ensembles can be directly manipulated, in particular when a catalytically active metal is diluted with a catalytically less active or inactive metal.[8]

A more recent approach that is showing increasing impact in catalysis research constitutes the use of organic molecules that are not soluble in the reaction medium and are strongly bound to the particle surface, also referred to as ligands, to control the catalyst selectivity.[9] Similar as incorporation of a second metal into a NP, the binding of ligands can electronically and geometrically alter the surface and, as a result, tune the catalytic properties.[10] However, in contrast to bimetallic NPs, the use of ligands is not restricted to modifications of the catalyst nature. In addition, interactions between the ligand shell and the reactants are possible.[11,12] In this way, the reactivity of certain functionalities can be inhibited parallel to the simultaneous increase of the reactivity of other functional groups.[13,14] This feature opens the possibility for a completely unexplored potential to tune and improve the chemoselectivity of supported catalysts in a way thus far only known for homogenous catalysts.[15] Even chiral information can be transferred from the ligand shell to the activated reactant,[16] which allows for stereoselective conversions. Supported ligand-functionalized catalysts with more than 80% enantiomeric excess for specific reactants have been recently reported.[12] Therefore, this relatively novel catalyst type is a significant contribution to the field of asymmetric catalysis by metal nanoparticles, which is currently dominated by (i) dispersed colloidal non-supported or supported NPs stabilized by phosphorous-based ligands known from homogeneous catalysis[17] and (ii) supported NPs covered with chiral modifiers, i. e. chiral molecules soluble in the reaction medium, especially chinchona alkaloids.[18]

Clearly, the key to utilize the enormous potential of ligands for supported catalysts is to understand the synergy between ligands and reactants and the way the interactions between the two can be utilized to tune catalyst selectivity. A fundamental question that needs to be answered in this context is: does the reactant interact with a single ligand molecule forming a 1:1 complex, which governs the stereochemistry of the product? Or does the ligand shell act as a collective entity, forming an environment that determines the molecular interactions with the reactant like, e.g., the cavities in the porous structure of a zeolite.[19] The later aspect would strongly hamper a rational catalyst design because lateral interactions between ligands, which are challenging to rationalize and predict, would play a dominant role in the control of selectivity. From a historical perspective, most groups have primarily tried to understand and control selectivity by assuming 1:1 ligand-reactant interactions rather than considering the ligand shell as an environment within which the reactant activation and conversion take place. However, experimental evidence supporting that molecular reaction control by ligands on NPs is determined by 1:1 ligand-reactant interactions is lacking.

Motivated by this problem and inspired by the success of groups from the field of homogeneous catalysis, we here present a study on so-called nonlinear effects (NLE) that probes 1:1 ligand-reactant interaction hypothesis as the selectivity controlling factor. Surprisingly, we have found that for most of the investigated ligand-reactant combinations the control of stereoselectivity seems to be primarily determined by a 1:1 ligand-reactant interaction. Based on this novel mechanistic insight, we further investigated the influence of small structural changes of the ligand on the stereoselectivity of the catalyst. Similar as in homogeneous catalysis, the stereoselectivity and, accordingly, the ligand-reactant interactions were found to be very sensitive to even small geometric variations in the ligand structure. Finally, we report new fundamental insights into the interaction of amino acid based ligands with Pt NPs. Evidence is presented that in the active form of the catalyst a cation is coordinated to the ligand's carboxyl group. This cation, which can be easily varied during the process of catalyst preparation, alters the ligand-reactant interaction, eventually allowing the tuning of the catalyst's stereoselectivity.

Results and Discussion

Validation of the 1:1 Stoichiometry for the Ligand-Reactant Interaction Model

We have previously introduced an interaction model for α-amino acid ligands and β-keto ester reactants that predicts the origin of stereoselectivity to be determined by a 1:1 ligand-reactant complex.[12,20] This model has been very effective for understanding the origin of stereoselectivity and giving guidance to enhance the asymmetric bias. However, experimental evidence has been missing to support the hypothesis that the selectivity of ligand-functionalized nanoparticle catalysts is mainly determined by 1:1 ligand-reactant complexes. In order to address this fundamental question, the presence of possible nonlinear effects (NLE) was explored. Testing for NLE is a sensitive tool in homogeneous catalysis to probe if stereoselectivity is determined by a 1:1 ligand-reactant complex.[21,22] For this purpose, NPs were functionalized with given mixtures of the R- and S-enantiomers of proline (PRO), *tert*-leucine (*tert*-LEU), and phenylglycine (PHG) (see Fig. 1 for structures) and then deposited onto γ-Al_2O_3. The supported ligand-functionalized Pt NPs, which are 1.2 ± 0.3 nm in size (determined previously by transmission electron microscopy),[14,16] were tested as catalysts for the hydrogenation of the simplest ß-keto ester methyl acetoacetate (MAA) and the sterically more demanding methyl 4,4-dimethyl-3-oxovalerate (MDOV) and ethyl 3-oxo-3-phenylpropanoate (EOPP) (see Fig. 1). The resulting enantiomeric excess (*ee*) of the product was plotted vs. the *ee* of the ligand used for functionalization of the NPs. A NLE is considered to be present if the resulting plot deviates significantly from a linear function.

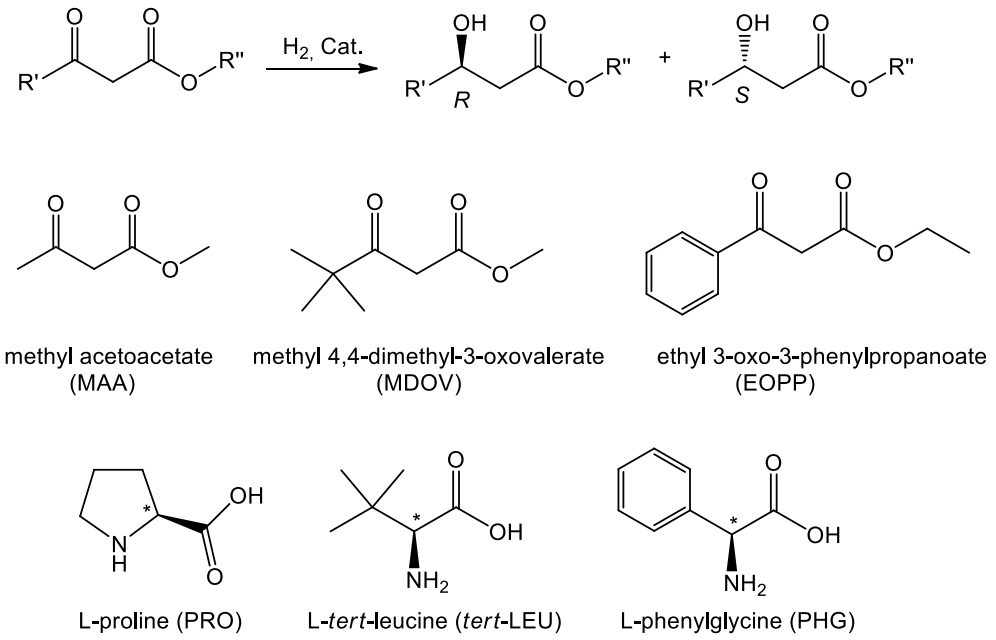

Figure 1. Catalytic hydrogenation process and structures of reactants and ligands.

Taking into account the preparation procedure of the ligand-functionalized Pt NPs and our so far achieved knowledge about the hydrogenation of ß-keto esters over these catalysts, there are likely three possible reasons for the occurrence of NLEs in these systems. The first concerns the catalyst structure only. The ratio of the two ligand enantiomers in solution, used to prepare the functionalized NPs, does not necessarily reflect the actual enantiomer ratio on the particle surface. Depending on the solvent and the ligand nature, aggregates may form due to ligand-ligand interactions. For example, the formation of ligand H-bonded dimers, a known phenomenon for carboxylic acids, can lead to three combinations RR, SS, and RS. While RR and SS are enantiomers that are hence energetically identical, RS is diastereomeric to RR and SS. As a result, RS exhibits a different energy than SS and RR. Although formation of H-bonded dimers of amino acids in our case is rather unlikely due to strong basicity of the media, similar processes may lead to enantiodiscriminative formation of other types of aggregates in the solution, e.g. micelles in the case of amino acids with lipophilic residues. This means that the ratio of "single, free" ligands can deviate from the total ratio in solution. Assuming that only "single, free" ligands can be bound to the NPs, but not dimers or aggregates, the resulting ligand *ee* on the particle surface will vary from that in solution. Moreover, on the NP surface adjacent ligands may interact with each other. Such lateral interaction will be sensitive to the ligand configuration and influence the overall energetics of the ligand shell formation. During functionalization the ligand shell with the lowest energy will be formed. If ligand-ligand interactions are strong, the ligand *ee* on the surface may certainly not be the same as that in solution.

The second reason for a NLE can be that the origin of enantiodifferentiation is not exclusively based on a 1:1 interaction complex of the reactant with a ligand. A 1:1 complex leads to two diastereomeric transition states. As these two interaction modes have different free energies, the overall reaction becomes stereoselective with the resulting *ee* being determined by the difference in free energy of the two transition states ($\Delta\Delta G^{\ddagger}$).[23] If, for instance, the two 1:1 ligand-reactant complexes experience a chiral environment such as an adjacent ligand or an adsorbed reactant (note that the adsorbed prochiral reactant is chiral due to its interaction with a ligand) they further change in energy. The resulting energy changes for the two states are however different as they become diastereomeric. This results in a nonlinearity for the product *ee* when plotted vs. the ligand *ee*. The stronger this plot deviates from linearity the more complex is the interaction of the reactant with the ligand shell. Additional insights in the structure of the catalytic active species reveal the consideration of curve shapes. Kagan et al. have developed mathematic models (ML_n where M is the metal center and L_n refer to n ligand molecules) for the calculation of curve shapes by taking into account the relative reactivity and the relative concentrations of homochiral and heterochiral complexes.[24,25] These models are helpful as a guide for the further interpretation of the observed NLEs.

The third possibility for a NLE is that the product ratio is not merely determined by two diastereomeric reaction pathways proceeding via two ligand-reactant complexes, but is also influenced by additional, completely different pathways. Since these other reaction pathways will show different dependencies for the product *ee* as the ligand *ee* on the surface is being varied, a very complex, unpredictable relation between product *ee* and ligand *ee* must be expected. Based on recent kinetic investigations, we can however exclude this possibility.

In homogeneous catalysis, the magnitude of NLEs depends strongly on the structure of reactant and ligand.[26] The possibility of deviations from a simple 1:1 ligand-reactant complex is expected to increase with complexity of the ligand and reactant. The results obtained for MAA, which is the smallest and least complex of the explored reactants, are hence discussed first (see Fig. 2).

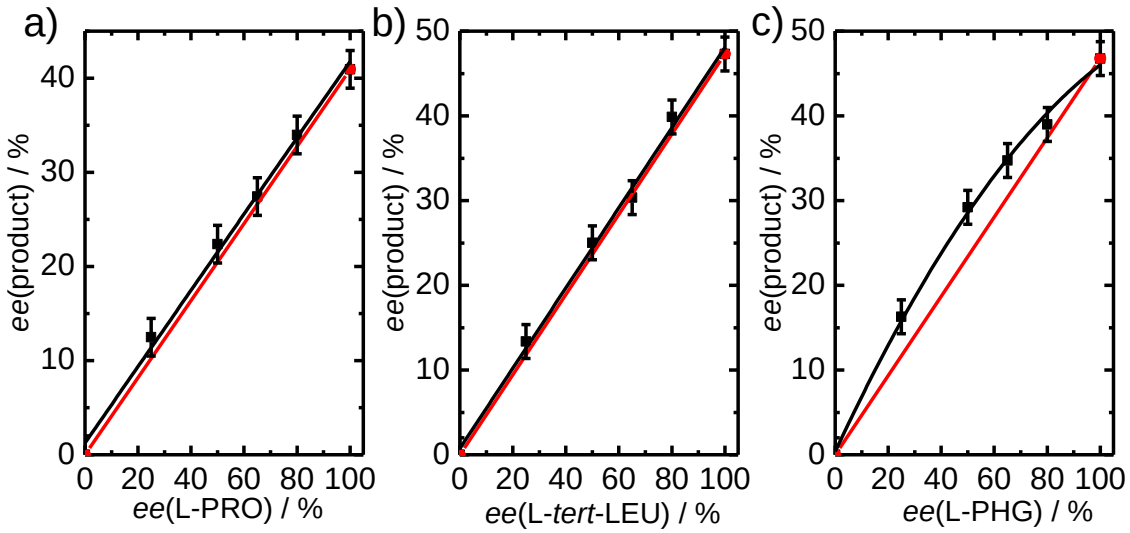

Figure 2. Relation between the product *ee* and the ligand *ee* for hydrogenation of MAA over Pt NPs functionalized with PRO (a), *tert*-LEU (b), and PHG (c). The solid lines are fits of the experimental data that serve merely as guides to the eye.

For PRO- and *tert*-LEU-functionalized Pt NP catalysts, the *ee* clearly shows a linear dependence and no NLE. We thus conclude for these materials: i) the ratio of the two ligand configurations on the surface does not vary from the ratio in the solution used to functionalize the NPs, ii) as expected, the hydrogenation of MAA seems to proceed via only two suggested diastereomeric reaction pathways that iii) are indeed determined by a 1:1 ligand-reactant interaction. For PHG-functionalized Pt NPs, a minor NLE is found. Given the fact that no NLE was obtained for MAA hydrogenation over the other two catalytic systems, we assume that in the case of PHG-functionalized Pt NPs the ratio of the two ligand configurations on the catalyst surface deviates from that used for the catalyst preparation. As above mentioned, such artifacts are expected to arise from ligand-ligand interactions in solution or

on the surface during preparation. In this context, the phenyl group may play a decisive role. Functionalization is performed in water, a very polar solvent that poorly solvates nonpolar groups (e.g. hydrocarbons, aromats). Likely, the hydrophilic phenyl substituents of PHG ligands may interact preferentially with each other (the strength of π-π-interactions is up to 12 kJ/mol for a pair of interacting benzene rings[27]), a phenomenon known from surfactants that drives the formation of micelles. Positive NLE effect (asymmetric amplification, higher product *ee* in relation to ligand *ee*) implies that the catalyst surfaces were modified by enantiomerically enriched ligand.

For hydrogenation of the very bulky reactant MDOV, no NLE is obtained over PRO-Pt NPs with respect to the limit of experimental accuracy, while for *tert*-LEU-Pt NPs a modest NLE is found (see Fig. 3).

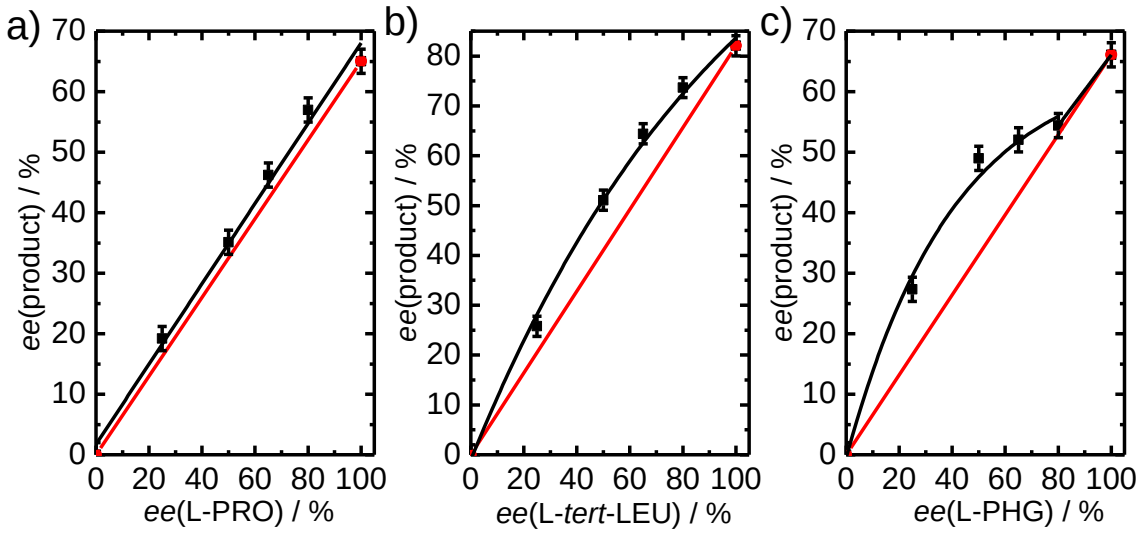

Figure 3. Relation between the product *ee* and the ligand *ee* for hydrogenation of MDOV over Pt NPs functionalized with PRO (a), *tert*-LEU (b), and PHG (c). The solid lines are fits of the experimental data that serve merely as guides to the eye.

MDOV is much bulkier reactant than MAA that exhibits a significantly greater steric demand than the latter due to *tert*-butyl group. This increases the probability of lateral interactions and in turn reduces the likelihood of a 1:1 ligand-reactant complex as the sole stereoselectivity determining factor. However, since the NLE for MDOV hydrogenation over *tert*-LEU-Pt NPs is only modest, enantiodifferentation still seems to be determined mainly by a 1:1 ligand-reactant complex. The simple symmetric curve shape suggests that additionally there are ligand-reactant complexes which interact with one adjacent ligand or reactant molecule (ML_2 model[24]). In homogeneous catalysis, London dispersion interactions are known to be an important stereoselectivity governing factor when utilizing bulky reactants and ligands.[28] In fact, it has recently been shown that such

interactions also play a decisive role for our catalytic systems when ligands and reactants with bulky alkyl substituents are applied.[12] We, therefore, assume that the slight deviation from a linear behavior may result from attractive van der Waals interactions (London dispersion) between the *tert*-butyl substituent of the reactant or ligand of the ligand-reactant interaction complex and second adjacent ligand or reactant molecule. For PHG-functionalized Pt NPs, a stronger deviation from a linear dependence is observed. This indicates that deviations from a 1:1 model may become significant. We have recently shown experimental evidence for the presence of π-π-interactions between aromatic ligands and reactants for the here discussed catalytic systems.[12] It is hence assumed that the increasing deviation from a 1:1 ligand-reactant interaction is driven by the presence of such π-π-interactions that may allow for lateral interactions with additional adjacent ligand or reactant molecules. An interesting aspect is the unconventional curve shape. There is clearly a positive NLE, but only until an ee value of 80% is reached for PHG ligand. Then a linear relationship occurs until enantiomerically pure PHG is used. A similar behavior has been reported for the asymmetric oxidation of sulfide in the presence of diethyl tartrate where a strong negative NLE was prevailing up to a value of 70%, but the linearity was regained by using diethyl tartrate of optical purity higher than 70%.[21] An explanation for this behavior may be interaction of some 1:1 ligand-reactant complexes with three adjacent ligand or reactant molecules (ML_4 model[24]), i.e. considering the configuration there are five possible combinations $(R)_4$, $(S)_4$, $(R)_3S$, $(S)_3R$, and $(R)_2(S)_2$. However, as concluded above for the reactant MAA, the ligand *ee* of PHG on the surface is expected to deviate from the ligand *ee* in solution. Hence, the stronger NLE for MDOV hydrogenation over PHG-Pt NPs compared to that over *tert*-LEU-Pt NPs is likely to result from two effects occurring in parallel. As the two effects cannot be distinguished from each other, we do not further stress the discussion of these results but rather conclude that this is the first of the here reported ligand-reactant combinations that shows a significant NLE.

The results obtained for the hydrogenation of EOPP over PRO-Pt NPs differ from those for the two other reactants (compare Fig. 4a to 2a and 3a). While no NLE was concluded for MAA and MDOV, a minor NLE is seen for EOPP. The effect is still small enough justifying the conclusion that the stereoselectivity is predominantly determined by a 1:1 ligand-reactant complex. However, the result reveals an interesting aspect considering the previously discussed results for PHG-functionalized NPs. It seems that the presence of phenyl substituents within the ligand or the reactant increases the probability of NLEs (see. Fig 2c and 3c), most likely due to π-π-interactions between the aromatic moieties.

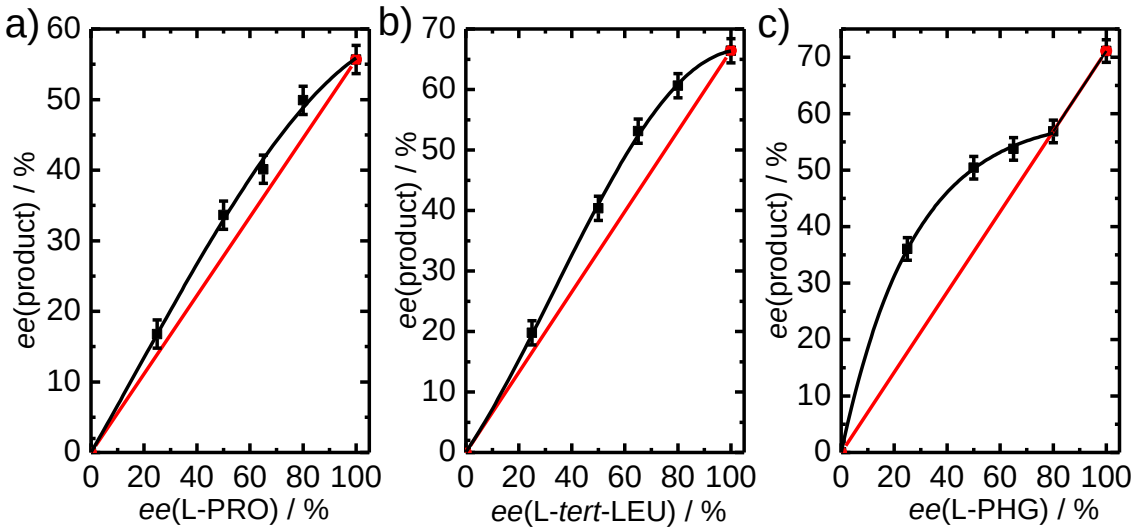

Figure 4. Relation between the product *ee* and the ligand *ee* for hydrogenation of EOPP over Pt NPs functionalized with PRO (a), *tert*-LEU (b), and PHG (c). The solid lines are fits of the experimental data that serve merely as guides to the eye.

The NLE of *tert*-LEU-functionalized Pt NPs is slightly more pronounced as that of PRO-Pt NPs, but still moderate. This implies that a 1:1 interaction is still sufficient to explain the asymmetric control for EOPP hydrogenation over these NPs. Interestingly, the NLE curves obtained for the hydrogenation of EOPP over PRO- and *tert*-LEU-Pt NPs are not symmetrical (i. e. the maximum is not at 50% *ee*). Such complicated curve shapes may originate from a lateral interaction of some of 1:1 ligand-reactant complexes with at least two further ligand or reactant molecules (ML_3 or ML_4 model[24]).

The NLE of PHG-functionalized Pt NPs is clearly more pronounced as those for PRO- and *tert*-LEU-Pt NPs, but as for MDOV we cannot deconvolute the contribution of the catalyst's surface ligand *ee*. We therefore do not further discuss the results obtained for PHG-Pt NPs in combination with EOPP.

To conclude, the NLE test experiments suggest that for ligands and reactants without bulky substituents, the sole stereoselectivity determining factor is 1:1 ligand-reactant interaction. For ligands and reactants possessing sterically demanding alkyl substituents, the stereoselectivity is still predominantly determined by a 1:1 ligand-reactant complex but effects due to lateral interactions of these 1:1 complexes with adjacent ligand or reactant molecules become evident. More pronounced NLEs and thus stronger deviations from 1:1 complexes as the stereoselectivity controlling factor are observed for ligands and reactants with phenyl substituents, likely due to the ability to build up π-π interactions. Furthermore, evidence was found that the presence of a phenyl substituent within the ligand influences even the catalyst preparation. As a result, the ligand *ee* on the particle surface deviates from that used for NP functionalization, which leads to complex systems and diminishes our predicting capacity for these systems.

Effect of Geometric Changes within the Ligand

As previously reported, ß-keto ester reactants and α-amino acid ligands are privileged combinations to achieve high stereoselectivities with supported ligand-functionalized NP catalysts. We could explain this selectivity by a 1:1 ligand-reactant interaction model, which has now been supported by NLE tests (see above). As demonstrated experimentally and by means of computational methods, amine bound hydrogen substituents become acidic as amines are bound to late d-metals (e.g. Pt). Such protons coordinate and activate ketones leading to an enhanced reaction rate.[29] An ester can coordinate in two ways to the ligand's N-H proton: either with the ester group being oriented towards the side of the ligand that binds the COOH group or vice versa, thus affording two diastereomeric adsorption modes (compare Fig. 7). The pronounced stereoselectivity, which can be achieved for β-keto ester reactants in combination with α-amino acid ligands, stems from the fact that in one of the two diastereomeric adsorption modes the reactant's ester group can interact with the ligand's carboxyl group. This leads to a so-called two-point binding and a stabilization of this adsorption mode compared to its diastereomeric counterpart. The stereoselectivity is determined by the difference in free energy ($\Delta\Delta G^{\ddagger}$) of the two transition states formed from these diastereomeric 1:1 adsorption complexes. An enhanced two-point binding mode will lead to a stronger enantiodifferentation.[20]

As the stereoselectivity is determined by molecular interactions between the ligand and the reactant, the *ee* should be sensitive to small changes in the geometry of the ligand-reactant interaction complex. In order to verify this hypothesis, a four- and a six-membered ring analogues to PRO were tested as ligands for Pt NPs (see Fig. 5 for structures). These three ligands exhibit quite similar steric demand, but due to ring tensions the distance and angle between the amino and the acid group differ, which may cause geometric variations within the ligand-reactant interaction mode.

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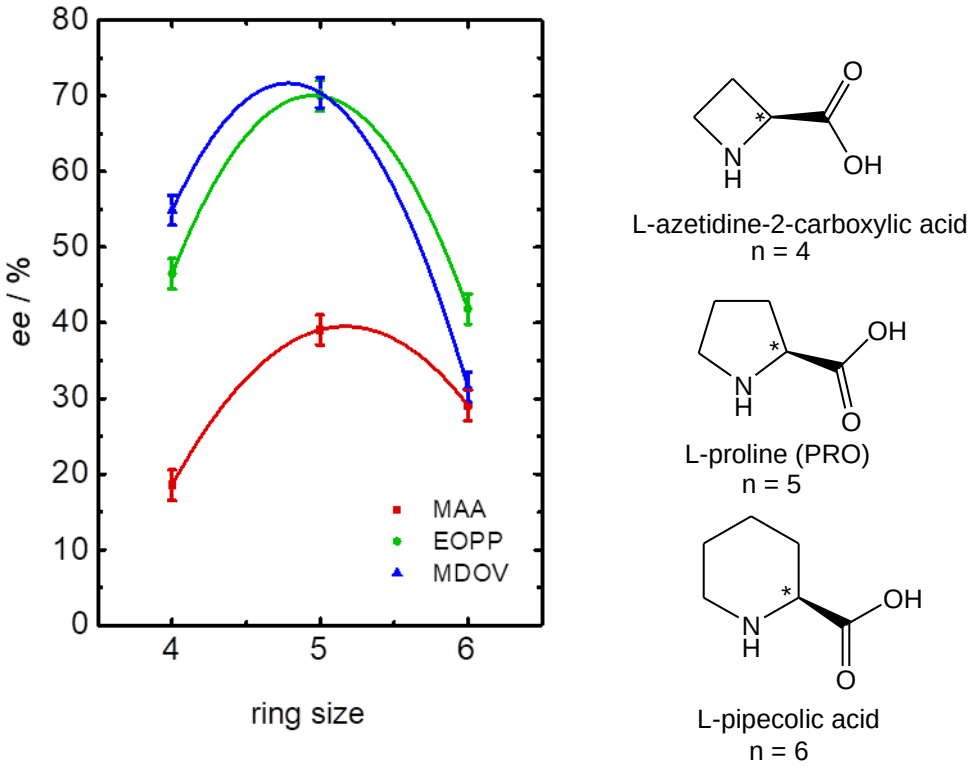

Figure 5. Effect of the ring size of the ligand on the stereoselectivity. Structures of the ligands are shown on the right. The solid lines are fits of the experimental data that serve merely as guides to the eye.

The obtained stereoselectivities (see Fig. 5) clearly show that PRO is the best ligand irrespective of the reactant structure. This seems reasonable considering the fact that PRO is also the best chiral organocatalyst used in multiple asymmetric transformations.[30] For example, List et al. have compared PRO with its four- and six-membered ring analogues in the direct asymmetric aldol reaction between acetone and a variety of aldehydes with the result that the pyrrolidine ring is essential for an efficient stereoselective conversion.[31] A further similarity to observations in organocatalytic reactions[32] is the fact that the ligand with six-membered ring shows a low sensitivity to steric bulkiness of the reactant unlike both other ligands, which produce much higher *ee* for the bulky reactants MDOV and EOPP than for MAA.

Therefore, the high deviations of the *ees* obtained for the hydrogenation of ß-keto esters over Pt NPs functionalized with PRO compared to its four- and six-membered ring analogues indicate that the ligand-reactant interaction and the resulting stereoselectivity are very sensitive to the distance and angle between the amino and the carboxyl groups of the ligand.

The Role of Alkali Metal Ions

The chemical form of amino acids can vary from neutral (NH_2RCOOH) to anionic (NH_2RCOO^-), to cationic (NH_3^+RCOOH), or to zwitterionic ($NH_3^+RCOO^-$), depending on the pH of the solution.[33] In aqueous solutions at pH = 7 amino acids appear as zwitterions with protonated amino group, which is lacking the free lone pair at the nitrogen required for coordination to the late transition metal surface.[34] Therefore, alkaline conditions are needed for the deprotonation of the NH_3^+ (or NH_2^+ in case of PRO) functionality. For aqueous solution of PRO, the pK_a value for the deprotonation of carboxyl group is 1.99, whereas the pK_a value for the deprotonation of the NH_2^+ group is 10.60. This means that the carboxyl group of the amino acid is already fully deprotonated, when the pH value becomes high enough for the deprotonation of the amino group. This trend generally holds for all amino acids.

We have recently showed that the pH of the functionalizing solution during the ligand functionalization step influences the catalytic properties of the resulting catalysts[12,20] and, thus, decided to further explore the state of the carboxylic group of the ligand. In our preparation procedure, ligand functionalization is performed under basic conditions and the supported ligand-functionalized Pt NPs are washed twice with ethanol to remove excess ligands. Successful removal of non-binding ligands was demonstrated by NMR spectroscopy.[14] In early studies, when only a rather low *ee* of 16% was obtained, we found this "preconditioning" of the as-prepared catalysts to be essential. When catalyst rinsing was performed with acetone the reaction turned out to be much less stereoselective. From this finding it was concluded that a protic solvent is of fundamental importance to achieve meaningful stereoselectivities, which may be related not only to the removal of excess ligands but also to removal of the excess NaOH and, possibly, partial re-protonation of the ligand's carboxyl group. For this reason, we thus far proposed in our ligand-reactant interaction model that the carboxyl group is protonated, which allowed us reasonable mechanistic understanding.

Since these early studies we intensively worked on the functionalization of the NPs to improve stereoselectivities and have achieved it with great success: *ees* of more than 80% are today feasible. However, both ligand and NaOH concentrations used in our present preparation procedure vary significantly from the initial recipe and are much higher (Δc(PRO) = 7.5 mM, Δc(NaOH) = 27.5 mM). This finding encouraged us to test the influence of catalyst rinsing prior to catalytic applications with acidic protic (acetic acid), protic (ethanol), and non-protic (acetone) solvents on the stereoselectivity (see Table 1). It is seen that the highest *ee* is reached by using catalysts rinsed with ethanol. The *ees* obtained for the hydrogenation over Pt NPs rinsed with acetic acid or acetone are significantly lower. In order to verify that the changes in stereoselectivity are not caused by a loss of surface-bound ligands during samples rinsing, the chemoselectivity of the hydrogenation of EOPP was investigated. This reactant possesses a phenyl group and a C=O group that may both undergo hydrogenation.

While PRO-Pt NPs are highly chemoselective toward the unsaturated alcohol (= exclusive hydrogenation of the C=O group), over "ligand-free" Pt NPs undesired hydrogenation of the phenyl substituent occurs resulting in a chemoselectivity of about 63% for the formation of the target unsaturated alcohol.[20] If any of the solvents used for the samples rinsing causes a removal of surface-bound ligands, a decrease in chemoselectivity was expected. For the hydrogenation of EOPP over PRO-Pt NPs rinsed with different solvents, the stereoselectivity shows a similar behavior as in the case of MAA (see Table 1) and a chemoselectivity of more than 99% is obtained without production of any side products. This indicates that changes in stereoselectivity are not caused by formation of ligand-free surface sites, but the surface remains densely covered with ligands.

Table 1. Sodium content of PRO-Pt NPs rinsed with different solvents and the corresponding enantioselectivity for the hydrogenation of MAA and EOPP. An experimental error of ±2% has to be taken into account for the *ee*. Additional, the Na^+/Pt molar ratio was calculated.

rinsing	Pt [wt%]	Na^+ [wt%]	Pt* [mol]	Na [mol]	Na^+/Pt	MAA *ee* [%]	EOPP *ee* [%]
2x ethanol	1.25	6.58	$3.95 \cdot 10^{-6}$	$2.08 \cdot 10^{-4}$	52.55	40	72
2x acetone	1.28	1.59	$4.37 \cdot 10^{-6}$	$5.43 \cdot 10^{-5}$	12.40	33	44
1x acetic acid, 1x ethanol	1.30	1.87	$4.19 \cdot 10^{-6}$	$6.03 \cdot 10^{-5}$	14.36	29	39
2x acetic acid, 1x ethanol	0.68	0.65	$2.89 \cdot 10^{-6}$	$2.76 \cdot 10^{-5}$	9.54	6	34

* ligand-functionalized Pt atoms taking into account that ligand coverage of PRO-Pt NPs is 85%

Our results show that ethanol is the best solvent for catalyst rinsing to obtain high stereoselectivities. Rinsing with acetic acid, which should be accompanied by at least partial reprotonation of the ligand's carboxyl group, leads to a decrease of the stereoselectivity. This implies that, in the case of our standard catalyst preparation procedure, the negative charge of the carboxyl group of the ligand is not balanced by a proton but presumably by Na^+ that originates from the NaOH used for functionalization. To test for this hypothesis, we determined the sodium concentrations of the PRO-Pt NPs rinsed with different solvents (see Table 1). It can be seen that the sodium content of catalysts rinsed with acetone or acetic acid is significantly lower than that of Pt NPs rinsed with ethanol. Thus, we conclude that the high Na^+ content of PRO-Pt NPs rinsed with ethanol is essential for reaching of a high *ee*. If the particles are rinsed with acetic acid, the sodium ions present in the catalysts are likely to be at least partially displaced with hydrogen, lowering its stereoselectivity. The second rinsing with acetic acid lowers also the platinum content of the catalyst, most likely due to the partial removal of Pt-NPs from the support, as the acetic acid turns dark after catalyst rinsing. On the other hand, the high molar content of sodium ions in the case of ethanol-washed catalyst indicates that,

beside Na^+ coordinated to COO^- group of the ligand, there should be excessive Na^+ content in the catalysts, which presumably resides on the support material.

To further test if the ligand actually exists in the form of a sodium salt on the metal surface, three different alkali metal hydroxides (LiOH, NaOH, and KOH) were tested during particle functionalization phase with PRO (see experimental section for details and see Fig. S1 for metal content in samples). Alkali metal cations are all singly charged, but they are clearly different in size. If the cation takes part in the ligand-reactant complex, change of the cation is expected to alter stereoselectivity. This hypothesis was probed by application of catalysts prepared with LiOH, NaOH, and KOH for the asymmetric hydrogenation of MAA.

Catalyst prepared from particles functionalized in the presence of NaOH led to a significantly higher *ee* than LiOH and KOH (see Fig. 6). This result indicates that the counter ion of the metal hydroxide used for the ligand functionalization process does not just remain a passive additive to the catalyst, but plays an important role in the enantiodifferentiating process. Hence, the ion must contribute to the ligand-reactant complex and, furthermore, its size plays a decisive role in the catalytic process. This fact clearly supports the hypothesis that the charge of carboxyl group is not balanced by a proton but by a cation originating from the metal hydroxide.

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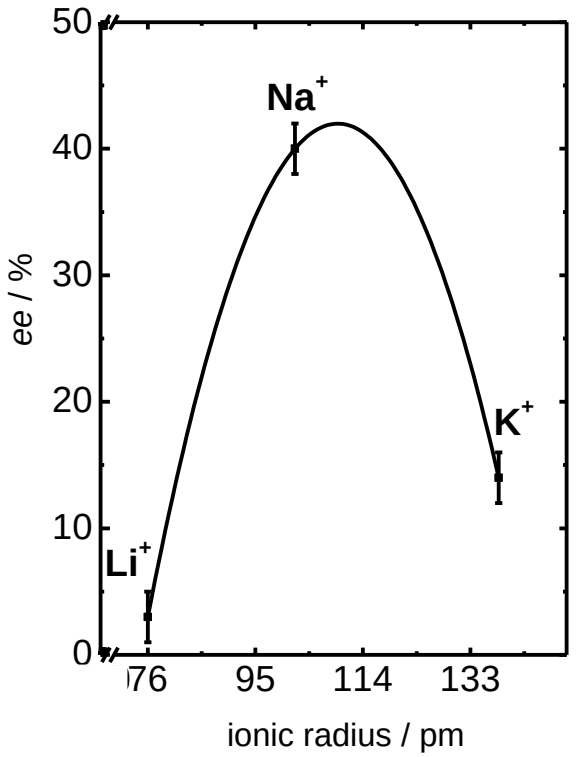

Figure 6. Effect of different alkali ions used for the functionalization of Pt NPs with PRO on the stereoselectivity. The solid line is a fit of the experimental data that serve merely as a guide to the eye. The ionic radii were taken from the literature.[35]

The functionalization of the Pt NPs is not the only preparation step where NaOH is present. Also the synthesis of "ligand-free" Pt NPs that are subsequently functionalized with PRO is performed in the presence of NaOH (see experimental section). To clarify that the cation being relevant for the enantiodifferentiation originates from the ligand functionalization step and not from the synthesis of the "ligand-free" NPs, we performed NP synthesis using LiOH followed by functionalization in the presence of LiOH-, NaOH-, and KOH-PRO-solutions. No difference in the *ees* was found if LiOH or NaOH were used for the synthesis (see Table S2). Accordingly, the cation used for the ligand functionalization step is essential for the control of the stereoselectivity, but not the cation applied for the synthesis of "ligand-free" NPs during the earlier stages of catalyst preparation.

Based on the above discussed experimental evidence that the carboxyl group is definitely not protonated but coordinates a cation to maintain the charge balance, our previously introduced model of reactant-ligand interactions should be modified accordingly. In previous studies, we proposed a hydrogen bond between the C=O group of the ester and the OH group of the amino acid.[12] However, as discussed above, it seems much more plausible that the deprotonated carboxyl group is counter balanced by Na^+ cation. As a result, the carboxylic group of amino acid and the C=O

group of the ester will attract the Na^+ cation by electrostatic interactions forming two-point binding complex (see Fig. 7a). This modification allows us to explain the strong variations of the stereoselectivity when Na^+ is replaced by either Li^+ or K^+. As shown above for varying the ring size of the ligands, the asymmetric bias is very sensitive to even small variations of bond lengths and angles. The diameter of a Li^+ cation is about 25% smaller than that of a Na^+ cation, while a K^+ cation exhibits a 26% greater diameter. Either changes, decrease or increase of cation size, may lead to destabilization of the two-point binding complex (Fig. 7a) compared to the ligand-reactant complex formed with Na^+. On the other hand, the diastereomeric binding mode (Fig. 7b) will not be strongly influenced by the metal cation. As a consequence, the free energy of the transition state formed from the two-point binding mode will increase, which in turn causes a decrease of $\Delta\Delta G^{\ddagger}$ and the *ee*, as the size of the cation is varied.

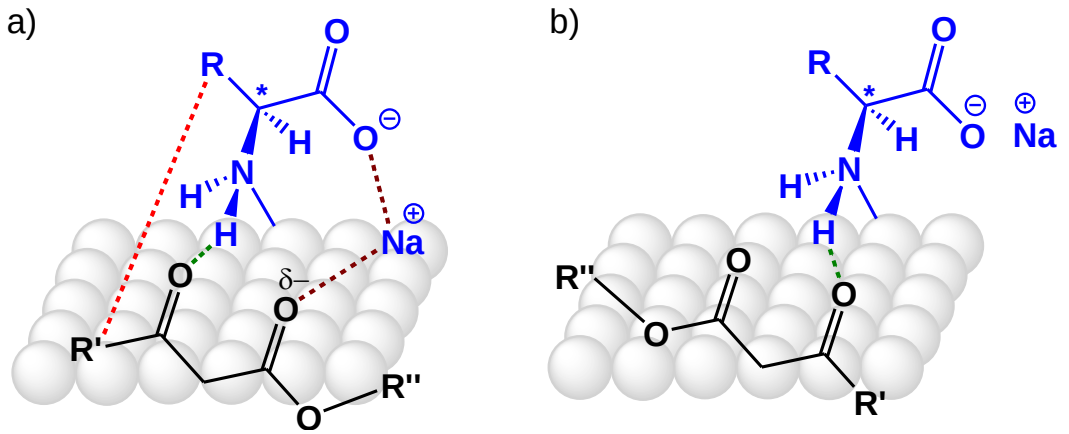

Figure 7. Ligand-reactant interaction model featuring two diastereomeric H-bonding interaction modes between α-amino acid (blue) and β-keto ester (black) on Pt NP surface (grey balls). The two-point binding mode (a, leads to the product with R configuration) is lower in free energy than the one-point binding mode (b, leads to the product with S configuration). Please note that the molecule of β-keto ester does not lie flat, but tilted to the surface and H_2 is attached from the "bottom" side of the molecule affording *R*-isomer for the two-point binding mode (a). Color codes for the attractive interactions: green – H-bonding interaction, red – London dispersion interaction between R substituent of the ligand and R' substituent of the reactant, brown – Coulombic interaction of sodium cation.

For the case of ß-keto esters, Na^+ seems to give the optimal fit between ligand and reactant. However, for other reactants a different cation size may be more beneficial for the asymmetric bias. If this holds, the choice of the cation may serve as an additional degree of freedom to fine-tune ligand-reactant interactions and, in this way, enantiodiscrimination. The first example where Li^+ was indeed found to be better for the asymmetric bias than Na^+ is the hydrogenation of the smallest α-keto ester methyl pyruvate (see Fig. 8).

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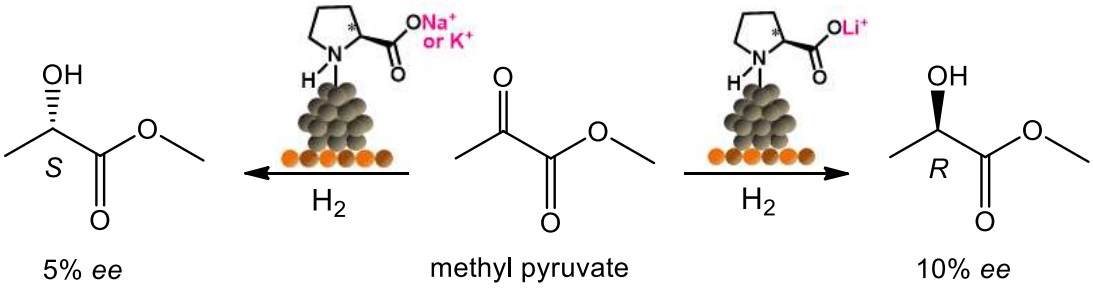

Figure 8. Hydrogenation of methyl pyruvate over PRO-functionalized Pt NPs coordinating different alkali metal cations.

If NaOH or KOH are used for the functionalization of Pt NPs with PRO, (S)-enantiomer of the product alcohol is primarily formed (*ee* = 5%). By using LiOH the configuration of the product is inverted from (S)- to the (R)-enantiomer and an *ee* of 10% is obtained. Even though *ees* are very modest, the results demonstrate the possibility to tune asymmetric biases by the variation of the cation. Further studies are in progress to find examples where Li^+ or K^+ will allow for a stronger enantiodiscrimination compared to Na^+.

Conclusions

In this work, we presented new fundamental insights into the ligand-reactant interactions in the asymmetric hydrogenation of ß-keto esters over α-amino acid-functionalized Pt nanoparticle catalysts. Previously, we proposed a 1:1 ligand-reactant interaction model. Now experimental evidence is provided from studies on nonlinear effects (NLE) that, at least in the absence of phenyl substituents, the stereoselectivity is indeed mainly determined by 1:1 ligand-reactant complexes. In contrast, introduction of a phenyl substituent within the ligand or the reactant leads to more complex systems with rather unpredictable NLEs.

We have demonstrated that the ligand-reactant interaction and the resulting stereoselectivity are very sensitive to small variations in distance and angle between the amino and the carboxyl groups of the ligand. Furthermore, we have presented evidence that the charge of the ligand's carboxyl group is balanced by coordinating to a metal cation. The nature of this cation plays a decisive role in the enantiodifferentiating process and we suppose that it may serve as an additional degree of freedom to fine-tune ligand-reactant interaction and in this way stereoselectivity of the catalyst. More detailed investigations to explore this hypothesis are currently in progress.

Experimental Section

Synthesis of "Ligand-Free" Pt Nanoparticles

"Ligand-free" Pt NPs were prepared according to a slightly modified protocol of the ethylene glycol (EG) method, first described by Wang et al.[36] In a 250 mL glass flask, $H_2PtCl_6 \cdot H_2O$ (0.25 g, 40% metal, ChemPur) was dissolved in ethylene glycol (25 mL, EG, ≥ 99.5%, Fluka) and a 0.5 M NaOH (99.6%, VWR) solution in EG (25 mL) was added. For specific experiments, the same amount of LiOH (98%, Alfa Aesar) was used instead of NaOH. The resulting mixture was vigorously stirred at 500 rpm and heated to 150°C using a preheated oil bath. After about 5 min the color of the solution changed from yellow to black indicating the formation of Pt NPs. To ensure quantitative reduction of the precursor, the reaction mixture was kept at 150°C for 1.5 h and then cooled to ambient temperature. The average particle size determined by transmission electron microscopy is 1.2 nm ± 0.3 and is maintained in all following preparation steps.[14,16] 1 M aq. HCl (50 mL, VWR) was added to precipitate the "ligand-free" Pt NPs. The precipitate was separated from the supernatant solvent by centrifugation and washed once with 1 M aq. HCl (50 mL). Finally, the Pt NPs were re-dispersed in cyclohexanone (100 mL, 99.9%, VWR).

Preparation of Ligand-Functionalized Pt NPs

For the functionalization of the "ligand-free" Pt NPs, a previously established phase transfer method was used.[16] First, alkaline aqueous ligand solutions were prepared. The ligand and NaOH concentrations needed for each ligand to obtain maximum stereoselectivity were determined previously.[12,20] In order to optimize the concentration of LiOH and KOH (≥85%, Roth), Pt NPs functionalized with L-proline at different hydroxide concentrations were tested for the hydrogenation of methyl acetoacetate (MAA, see Fig. 1 for structure). The ligands and concentrations used are: L-*tert*-leucine (*tert*-LEU, > 98%, TCI) with 20 mM NaOH and 16 mM ligand, L-phenylglycine (PHG, 99%, Acros Organics) with 30 mM NaOH and 22 mM ligand, S-(-)-azetidine-2-carboxylic acid with 40 mM NaOH and 16 mM ligand, L-Pipecolic acid with 50 mM NaOH and 16 mM ligand, and L-proline (PRO, > 99%, TCI) with 40 mM NaOH, 40 mM LiOH or 30 mM KOH and 16 mM ligand (see Fig. 1 for ligand structures). The ligand solution (400 mL) was added to the previously prepared dispersion of Pt NPs in cyclohexanone (100 mL). This gives a ligand-to-Pt ratio of 12.3 – 16.9, depending on the particular ligand, to ensure saturation of the particle surface with ligands. The resulting two phase mixture was vigorously stirred. The stirring time needed for a successful phase transfer of the particles from the organic into the aqueous phase is 1 h for Pt NPs functionalized with PRO and its analogs and 1.5 h for *tert*-LEU- and PHG-Pt NPs.[12] During this mixing, the initially black organic phase turned clear while the aqueous phase became black. The black aqueous phase that contains the ligand-functionalized NPs was separated from the organic phase in a separation funnel.

Deposition of Ligand-Functionalized Pt NPs

For the deposition of the as-prepared Pt NPs onto support material, Al_2O_3 (Puralox SCCa 150/200; Sasol, grain size = 200-500 µm) was added to the particle dispersion to give a nominal metal loading of 2 wt%. The solvent was removed using a rotary evaporator (p = 20 mbar; T = 45°C). The supported ligand-functionalized Pt NPs were rinsed with ethanol (99.9%, VWR) two times to remove free ligands, dried under vacuum for about 2 min, and then applied for catalytic experiments. For specific experiments, acetic acid (99%, VWR) or acetone (99.9%, VWR) were used for samples rising.

In order to determine the actual Pt loadings of the catalysts, the samples were digested with freshly prepared aqua regia and analyzed by atomic absorption spectroscopy (AAS, Carl Zeiss Technology AAS 5 FL). The Pt loading is approximately 0.6 wt% Pt for PHG-Pt NPs and 1.2 wt% for Pt NPs functionalized with other ligands used in this work. For specified samples, also the sodium and potassium content was determined. Experimental capabilities to determine the lithium were not available.

Catalytic Hydrogenation

Hydrogenation experiments of methyl acetoacetate (MAA, 99%, Sigma Aldrich), methyl 4,4-dimethyl-3-oxovalerate (MDOV, >95.0%, TCI), ethyl 3-oxo-3-phenylpropanoate (EOPP, ≥97.0%, Sigma Aldrich), and methyl pyruvate (MP, >97%, TCI) were carried out in five in-house designed stainless steel autoclaves. The autoclaves were connected to the same H_2 (Linde 5.0) gas line and the same thermostat in order to perform five catalysis experiments with different reactants and/or catalysts in parallel under identical experimental conditions. In a typical experiment each autoclave was loaded with dioxane (9 mL, ≥99.9%, Carl Roth), reactant (1 mL) and catalyst (0.2 g). The autoclaves were flushed three times with hydrogen and filled to a pressure of 20 bar. The experiments were performed at a temperature of 293 K and at a stirring rate of 800 rpm. A stirring speed of 800 rpm was determined to be required to eliminate artifacts that may arise from external diffusion limitations. After the catalysis experiment (≥ 19 h for full conversion), the reaction mixtures were centrifuged to separate the liquid-phase products from the catalyst. We have seen by carrying out experiments for our previous publications[12,20] that for all ligands and reactants investigated in this work the *ee* does not vary in a conversion range of 1 to 100%.

Product Analysis of Catalytic Experiments

The reaction mixtures were analyzed by a gas chromatograph (Perkin Elmer GC-Clarus 580) equipped with a flame ionization detector (FID). For the analysis, the samples were diluted in 1:2 ratio with acetone (99.9%, VWR). Injections were performed at 200°C with Helium (Linde, 5.0) as carrier gas.

In order to determine the enantiomeric excess (*ee*), a Lipodex E column (Macherey-Nagel, 27 m length, 0.25 mm inner diameter, 0.25 µm film thickness) was used. Prior to analyzing the hydrogenation product of MDOV the samples were derivatized with *N*-methylbis(trifluroacetamide) (25 µL, 97%, abcr) at 60°C for about 4 h. For the *ee* determination of MAA and MDOV, the GC oven was held at 85°C for 20 min, then heated to 180°C at a rate of 30°C min^{-1} and kept at this temperature for 10 min. For the *ee* determination of EOPP the oven temperature was held at 80°C for 5 min and then increased to 139°C at a rate of 0.5°C min^{-1}. After further heating to 180°C at a rate of 30°C min^{-1} the temperature was held for 11 min. For the *ee* determination of MP, the oven was held at 70°C for 20 min, then heated to 180°C at a rate of 30°C min^{-1} and kept at this temperature for 10 min.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Ligand-functionalized nanoparticles, ligand-reactant interactions, nonlinear effects, selectivity control, stereoselective heterogeneous catalysis.

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