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COMMUNICATION

Effector enhanced enantioselective hydroformylation†

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In this communication, we report rhodium DIMPhos complexes with an integrated DIM-receptor that can bind carboxylate containing effectors and their application in the rhodium catalyzed hydroformylation reaction. The binding of chiral effectors in non-chiral [Rh(DIMPhos)] catalysts does not lead to enantioselective hydroformylation, but the binding of either achiral or chiral effectors can significantly enhance the enantioselectivity induced by the chiral Rh-metal complexes. For example, the supramolecular complex [Rh]/[1S⊂L3] displays high regio- and enantioselectivity in the hydroformylation of vinyl acetate (72% ee, and b/l >99), whereas in absence of this effector the ee is around 17%.

The hydroformylation reaction, also known as the oxo-process, enables the addition of a formyl group and a hydrogen atom to a C=C double bond using syngas (H$_2$/CO) to produce aldehydes with 100% atom economy.[1] Hydroformylation is one of the largest industrially applied homogeneous catalytic reactions, with applications in both bulk and fine chemical industry.[1] A lot of research focuses on achieving sufficient regio- and/or enantio-selectivity for the hydroformylation of a wide variety of substrates, which is also important for commercial applications. Particularly, the enantioselective hydroformylation is challenging but provides interesting entries to make fine chemicals, agrochemicals, fragrance and pharmaceuticals when a proper process can be developed.[2] BOBphos,[3] Binaphos,[4] Yangphos[5] and bis-3,4-Diaza-phospholane[6] are a few representative chiral ligands that are successful in this transformation.[2,7] Next to the traditional ligand modification, we are interested in exploring alternative approaches to optimize catalysts for this reaction.

Previously, we[8] reported DIMPhos (L1) as a diphosphine ligand with an integrated anion receptor (DIM-receptor). Rhodium complexes of this ligand can convert anion functionalized

alkenes with very high regio-selectivity as a result of substrate preorganization. In addition, we demonstrated that the binding of chiral effectors in the pocket of L1 results in chiral complexes that were highly enantioselective hydrogenation catalysts.[9] In addition, the palladium complexes of analogues ligands were successfully used in the effector controlled asymmetric allylic substitution.[10,11] We were wondering if similar effector controlled catalysis would be a useful strategy for the asymmetric hydroformylation reaction. Herein, we report the exploration of a series of DIM-based rhodium catalysts, ParaDIMPhos (L1)-rhodium catalyst, tropos DIMPhosphite (L2)-rhodium catalyst, and chiral DIMPhosphite (L3)-rhodium catalyst (Fig. 1) in the effector controlled asymmetric hydroformylation. These catalysts are all furnished with the DIM-receptor for the binding of effectors, by which the regio- and enantioselectivity in the hydroformylation can be controlled.
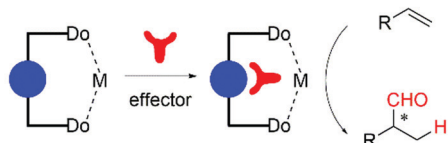
The DIM-ligands (L1–3) were prepared by following straightforward synthetic procedures based on previously developed protocols[8] and were fully characterized by NMR and HR-MS spectroscopy (see ESI†). We initially applied these rhodium catalysts in the hydroformylation reaction in the presence and absence of effector 1S, which was the effector that gave the best results in the asymmetric hydrogenation reaction.[9] The selectivity and conversion were determined by GC and ^{1}H NMR analysis. In the hydroformylation of styrene in the presence of 1S, all three catalysts [Rh]/[1S⊂L1–3] produce the aldehydes in close to racemic form. The branched aldehyde is the dominant product formed (b/l ratio around 15), which is typical in the hydroformylation of styrene (Table 1, entries 1–3). We next performed the hydroformylation of vinyl acetate, which has a functional group that can form hydrogen bonds with effector 1S (carbonyl–O hydrogen bonding with thiourea–NH), which was demonstrated to be important for the high enantioselectivity in effector controlled enantioselective hydrogenation reactions.[9] ParaDIMPhos (L1)-rhodium and DIMPhosphite (L2)-rhodium catalysts also gave racemic aldehydes when performing the hydroformylation of vinyl acetate in the presence of 1S (Table 1, entries 4 and 5). Interestingly, DIMPhosphite (L3)–rhodium catalyst displayed

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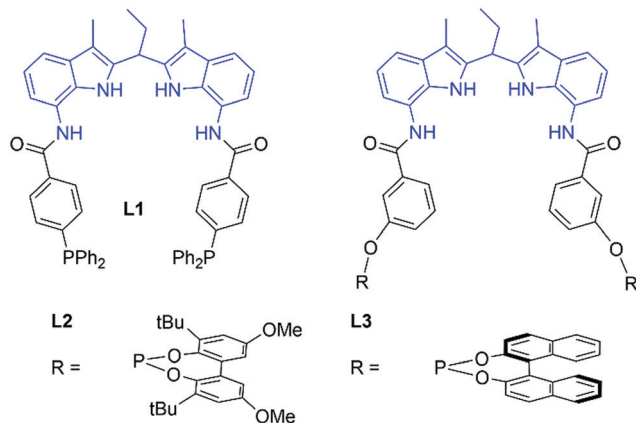
Fig. 1 (a) General concept of effector enhanced enantioselective hydroformylation; (b) DIM-type ligands studied in this contribution. The DIM-receptor is colored in blue.

Table 1 Asymmetric hydroformylation using DIM-ligands **L1–L3** and effector **1S**[a]

Entry	Substrate	Ligand	Effectors	Conv./%	ee[c]/%	b/l
1	Styrene	**L1**	**1S**	70	0	13
2	Styrene	**L2**	**1S**	100	1	15
3	Styrene	**L3**	**1S**	100	3	15
4	Vinyl acetate	**L1**	**1S**	16	1	3.3
5	Vinyl acetate	**L2**	**1S**	98	0	15
6	Vinyl acetate	**L3**	**1S**	55	65(R)	>99
7	Vinyl acetate	**L3**	—	100	1	>27
8[b]	Vinyl acetate	**L3**	**1S**	72	72(R)	>99
9[b]	Vinyl acetate	**L3**	—	26	17(R)	>99

[a] Conditions: 0.5% cat. [Rh(acac)(CO)$_2$]/**L** = 1/1.3, 0.2 M substrate, 10 mol% effector, 8 mol% DIPEA, 1 ml toluene as the solvent, 40 bar syngas, 40 °C, 96 hours. Conversion and regioselectivity were determined by ^{1}H NMR analysis. ee was determined by chiral-GC analysis. [b] Reaction was performed at room temperature, 120 hours. [c] Reported stereo-configurations were referred to the literature.[6f,12]

pronounced enantioselectivity and regioselectivity in the presence of **1S**, whereas in the absence of **1S** the product is formed in almost racemic form (65 vs. 1% ee and b/l >99 vs. 27, Table 1, entries 6 and 7). These results reveal that effector binding can indeed enhance the enantioselectivity and regioselectivity in the hydroformylation reaction. Importantly, even a higher enantioselectivity (72 vs. 65% ee, Table 1, entries 6 and 8) was achieved when the reaction was performed at room temperature instead of 40 °C.

Next, we extended the substrate scope to other vinyl derivatives using the supramolecular catalyst [Rh]/[**1S**⊂**L3**]. This catalyst displayed decent enantio- and regioselectivity in the hydroformylation of vinyl benzoate and vinyl pivalate (59 and 45% ee, respectively), and the regioselectivity was high for all substrates (b/l > 99%). In the absence of an effector, the DIMPhosphite-rhodium catalyst ([Rh]/[**L3**]) provided the products in a much lower ee (7–24% ee, Table 2, entries 2, 4 and 6). Also, [Rh]/[**1S**⊂**L3**] displayed much higher enantioselectivity than [Rh]/[**L3**] in the hydroformylation of N-vinyl phthalimide (25 vs. 1% ee, Table 2, entries 7 and 8). These experiments show that the effector has an effect on the catalyst properties when converting various substrates with different size and electronic properties.

We then performed catalytic experiments using a variety of both chiral and achiral effectors in the hydroformylation of vinyl acetate (Table 3). The catalyst in the presence of **1R**, which is the opposite enantiomer of **1S**, displayed the same stereochemistry and gave similar ee (72 vs. 68% ee, Table 3, entries 1 and 2), indicating that the chirality of the effector has little influence on the enantiomeric excess of the products. Interestingly, the reactivity is different when the effectors with R or S configuration are applied (conversion 72 vs. 37%, Table 3, entries 1 and 2), revealing that the effectors do affect the overall process via matched/mismatched effects. In line with this, control experiments in the presence of racemic effectors **1R/S** displayed the same stereo-outcome and intermediate activity (71% ee, conversion 56%, Table 3, entry 3). Interestingly, the catalyst system in the presence of achiral Fmoc-glycine increased the ee of the products formed, resulting in decent enantioselectivity (40% ee, Table 3, entry 4). Even the catalyst in the presence of a simple acetate as an effector gave much higher enantioselectivity than that in the absence of an effector (37 vs. 17% ee, Table 3, entry 5 and Table 2, entry 2). The catalyst in the presence of benzoate as an effector showed even higher enantioselectivity (58 vs. 37% ee,

Table 2 The substrate scope using [Rh]/[**L3**] as the catalyst and effector **1S**[a]

Entry	Substrate	Ligand	Effector	Conv./%	ee[b]/%	b/l
1	Vinyl acetate	**L3**	**1S**	72	72(R)	>99
2	Vinyl acetate	**L3**	No	26	17(R)	>99
3	Vinyl benzoate	**L3**	**1S**	69	59(S)	>99
4	Vinyl benzoate	**L3**	No	31	24(S)	>99
5	Vinyl pivalate	**L3**	**1S**	36	45(R)	>99
6	Vinyl pivalate	**L3**	No	71	7(R)	>99
7	N-Vinyl phthalimide	**L3**	**1S**	74	25	>99
8	N-Vinyl phthalimide	**L3**	No	74	1	>99

[a] Conditions: 0.5% cat. [Rh(acac)(CO)$_2$]/L = 1/1.3, 0.2 M substrate, 10 mol% effector, 8 mol% DIPEA, 1 ml toluene as the solvent, 40 bar syngas, room temperature, 96–120 hours. Conversion and regioselectivity were determined by ^{1}H NMR analysis. ee was determined by chiral-GC and HPLC analysis. [b] Reported stereo-configurations were referred to the literature.[6f,12]

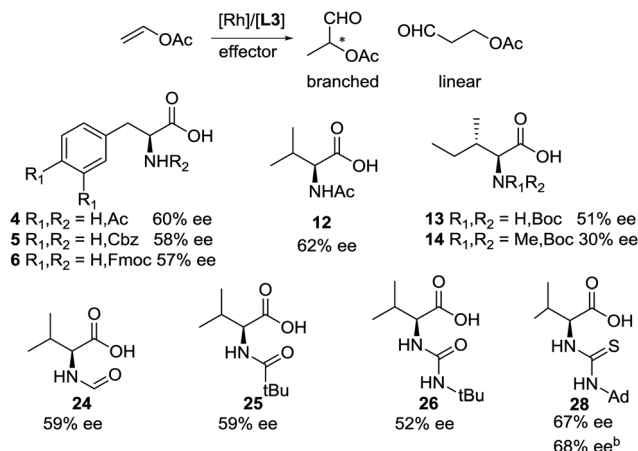**Table 3** Various catalysis experiments using chiral and achiral effectors[a]

Entry	Substrate	Ligand	Effectors	Conv./%	ee[b]/%	b/l
1	Vinyl acetate	**L3**	**1S**	72	72(R)	>99
2	Vinyl acetate	**L3**	**1R**	37	68(R)	>99
3	Vinyl acetate	**L3**	**1R + 1S**	56	71(R)	>99
4	Vinyl acetate	**L3**	Fmoc-glycine	21	40(R)	>99
5	Vinyl acetate	**L3**	Acetate	37	37(R)	>99
6	Vinyl acetate	**L3**	Benzoate	57	58(R)	>99
7	Vinyl benzoate	**L3**	Benzoate	40	47(S)	>99
8	Vinyl pivalate	**L3**	Benzoate	30	33(R)	>99
9	N-Vinyl phthalimide	**L3**	Benzoate	81	21	>99

[a] Conditions: 0.5% cat. [Rh(acac)(CO)₂]/L = 1/1.3, 0.2 M substrate, 10 mol% effector, 8 mol% DIPEA, 1 ml toluene as the solvent, 40 bar syngas, room temperature, 96–120 hours. Conversion and regioselectivity were determined by ¹H NMR analysis. ee was determined by chiral-GC and HPLC analysis. [b] Reported stereo-configurations were referred to the literature.[6f,12]

Scheme 1 Application of various effectors in [Rh]/[**L3**] catalyzed asymmetric hydroformylation. Conditions: 0.5% cat. [Rh(acac)(CO)₂]/L = 1/1.3, 0.2 M substrate, 10 mol% effector, 8 mol% DIPEA, 1 ml toluene as the solvent, 40 bar syngas, 40 °C, 96–120 hours. Conversion and regioselectivity were determined by ¹H NMR analysis. ee was determined by chiral-GC analysis. [b]Reaction was performed at room temperature.

Table 3, entry 6). Importantly, the [Rh]/[**L3**] catalyst in the presence of benzoate also displayed decent enantioselectivity for other studied substrates such as, vinyl benzoate, vinyl pivalate, and N-vinyl phthalimide (21–58% ee, Table 3, entries 6–9).

Next, we explored a large library of amino acids as effectors in the hydroformylation of vinyl acetate by performing parallel reactions under identical conditions (effectors **2–23**, Scheme 1 and Scheme S3 and Table S1, ESI†). Most of these catalyst systems with these effectors gave the products with an enantioselectivity higher than 55% ee. The catalysts in the presence of effector **4** and **12** with phenylalanine and valine backbone, respectively, showed enantioselectivity higher than 60% ee. Importantly, in the presence of effector **13**, the catalyst gave much higher selectivity than the catalyst in the presence of **14** (51 vs. 30% ee), suggesting that hydrogen bonds between vinyl acetate and **13** may be also involved in this effector controlled reaction as was previously observed for the DIM-effector controlled hydrogenation reaction.[9b] Also, catalytic experiments in the presence of a mixture of effectors displayed higher enantioselectivity than experiments in the absence of any effectors (24–55 vs. 1% ee, Scheme S3 and Table S2, ESI†). Detailed comparison with the single effector experiments show that in the presence of a mixture of effectors the result is roughly a linear combination of the different single experiments. So in contrast to observed for the asymmetric hydrogenation, the catalysis is not dominated by one of the effectors.[9]

In an attempt to obtain more selective catalysts, we further modified the effectors (Scheme 1). The catalyst with urea derivative **26** displayed lower enantioselectivity than amide derivatives **24–25** (52 vs. 59% ee). Also, the more bulky effector **25** and dipeptide effector **27** (Scheme S5, ESI†) do not lead to higher selectivity compared to **24**. On the other hand, a slightly higher enantioselectivity was achieved in the presence of the more bulky thiourea based effector **28** at 40 °C, compared to the

experiment with effector **1S** (67 vs. 65% ee). Performing the hydroformylation with effector **28** at room temperature slightly improved the enantioselectivity to 68% ee (Scheme 1).

In conclusion, we explored the binding of effectors to DIM-receptor based ligands and the properties in rhodium catalysed asymmetric hydroformylation. The use of non-chiral catalyst in combination with chiral effectors did give the aldehyde product in racemic form. The chiral catalyst in presence of an effector [Rh]/[**1S**⊂**L3**] displayed highly increased enantioselectivity (up to 72% ee) in the hydroformylation of N-vinyl phthalimide, vinyl acetate and its derivatives compared to catalyst systems in the absence of an effector. Also the use of non-chiral effectors and amino acids based effectors were shown to be effective leading to enantioselective hydroformylation of vinyl acetate with selectivities up to 68% ee. The in situ assembly of supramolecular catalysts using an effector approach provides a new tool which may be used to solve challenging selectivity issues in the field of transition metal catalysis.

Conflicts of interest

There are no conflicts to declare.

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