Hydroformylation of functional alkenes with heterodonor phosphine rhodium catalysts: substrate or ligand directed regioselectivity?

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The catalytic activity and selectivity of heterodonor phosphine rhodium catalysts prepared *in situ* were tested in the hydroformylation of functional alkenes (ethyl acrylate, methyl methacrylate, styrene, 4-vinyl-1-cyclohexene, dicyclopentadiene and *cis*-1,2,3,6-tetrahydrophthalic anhydride). Systematic variation of the heterodonor atom in the *ortho* position of the ligand showed that the heterodonor atom has a significant influence on the activities and selectivities of the reaction. However, the activity seems to depend mainly on the modifying ligand, and the regioselectivity mainly on the substrate (i.e., the structure and functionality of the alkene). Nevertheless, regioselective control is only obtained through synergy between the substrate and the catalyst. Clear regiocontrol was observed in the hydroformylation of α,β-unsaturated esters and styrene with an *in situ* formed *o*-(thiomethylphenyl)diphenylphosphine rhodium catalyst.

Keywords: heterodonor ligands, α,β-unsaturated esters, styrene, hydroformylation, substrate effect

1. Introduction

The hydroformylation reaction between the double bond in alkene and a mixture of hydrogen and carbon monoxide leads to linear and branched aldehydes as primary products. The aldehydes formed in the hydroformylation reaction serve as raw materials for a wide variety of bulk and speciality chemicals [1–5]. So far the emphasis has been on the selective production of linear products, even though from the synthetic point of view branched products appear to be more interesting and useful [6]. The most effective way to influence the selectivity of the rhodium-catalysed reaction is through a modifying ligand. Thus, the challenge in ligand synthesis is to understand structure–activity relationships well enough that the ligand can be tailored to favour the desired end product.

The stereoelectronic factors of the transition state determine the rate and the selectivity of the reaction. The properties of the transition state in turn depend not only on the organometallic metal centre or the properties of the ligands bound to it, but also on the functionality and geometry of the reacting alkene, as shown by Laï and Ucciani already in the 1970s [7]. Extensive studies have been made on phosphines and their coordination chemistry [8], and in some cases the catalytic results are adequately explained by the geometry of the ligands, for example, in the hydroformylation of α-alkenes with diphosphines the natural biting angle of the ligand correlates with the regioselectivity [9,10]. Still today, a satisfactory explanation of the role of the alkene has yet to be provided, and empirical determination of structure–activity relationships continues to be the most reliable method to estimate the catalytic potential of a complex with a particular substrate.

Systematic variation of the heterodonor atom in the *ortho* position of a triphenylphosphine ligand in rhodium-catalysed methyl methacrylate (MMA) hydroformylation [11] showed that the heterodonor atom has a significant influence on the initial reaction rates and selectivities of the reaction. The role of the functional alkene, MMA, in the regioselective control remained obscure. To clarify the role of the alkene structure and the properties of the reacting double bond and to further study the relationships between ligand structure and catalytic activity and selectivity, we studied the effect of *in situ* formed *o*-(thiomethylphenyl)diphenylphosphine (SP), *o*-(methoxyphenyl)diphenylphosphine (OP) and *o*-(N,N-dimethylaminophenyl)diphenylphosphine (NP) rhodium catalysts on the hydroformylation of various substrates (scheme 1). α,β-unsaturated esters, ethyl acrylate and methyl methacrylate, were chosen as substrates because of their polar and conjugated double bonds as well as for the presence of the ester group. Styrene and 4-vinyl-1-cyclohexene were chosen as an example of substrates with similar geometry but different functionality. Dicyclopentadiene and *cis*-1,2,3,6-tetrahydrophthalic anhydride were chosen on the basis of their internal cyclic double bonds, and *cis*-1,2,3,6-tetrahydrophthalic anhydride also for the presence of the anhydride group.

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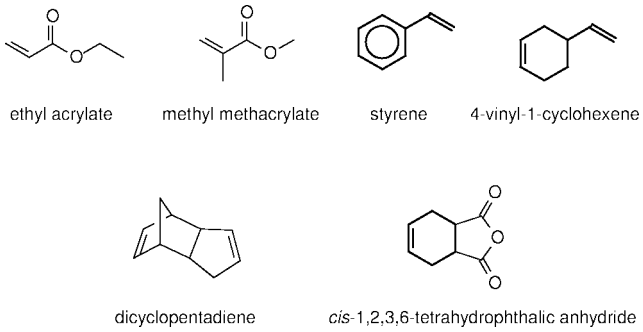


Scheme 1. Substrates used in the hydroformylation tests.

2. Experimental

2.1. Ligands

The structures of the ligands are shown in scheme 2. The preparation of the ligands *o*-(thiomethylphenyl)diphenylphosphine (SP), *o*-(methoxyphenyl)diphenylphosphine (OP) and *o*-(N,N-dimethylaminophenyl)diphenylphosphine (NP) is described in detail elsewhere [11]. Ligand purity (>95%) was checked by ^{1}H-NMR. Triphenylphosphine was used as a reference ligand (Fluka, 99%). Commercially available reagents were used without further purification.

2.2. Hydroformylation procedures

2.2.1. Ethyl acrylate, MMA and styrene

The hydroformylation experiments were carried out in a 250 ml autoclave (Berghof) equipped with a sampling system. The experiments were done in semi-batch mode so that synthesis gas pressure was kept constant during the experiment. A disposable Teflon liner was used to avoid the accumulation of rhodium on the reactor walls. Furthermore, the purity of the system was checked with blank runs after each experiment.

In a typical experiment the reactor was charged with $Rh(NO_3)_3$ (6.5 mg, Fluka), substrate (ethyl acrylate (5 g, Fluka, >99%), MMA (5 g, Merck, >99%) or styrene (5 g, Fluka, >99%)), toluene (18 g, Riedel de Häen, >99.7%) and the respective phosphine. The ligand to rhodium ratio was 4 : 1 if not otherwise stated. The system was flushed with nitrogen and heated to the reaction temperature (100 °C for ethyl acrylate and MMA and 80 °C for styrene) with continuous stirring, and then pressurised to reaction pressure (60 bar for ethyl acrylate and MMA and 20 bar for styrene) with a 1 : 1 molar ratio of H_2 and CO. Four samples were taken for analysis in each experiment: one immediately after pressurising with H_2 and CO, which was considered as the starting point of the reaction, and one after every first, third and fifth hour.

2.2.2. 4-vinyl-1-cyclohexene, dicyclopentadiene and cis-1,2,3,6-tetrahydrophthalic anhydride

The hydroformylation experiments were carried out in a 50 ml autoclave. The experiments were done in semi-batch mode so that synthesis gas pressure was manually kept constant during the experiment. A disposable Teflon liner was also used in this reactor, and the purity of the system was checked with blank runs after each experiment.

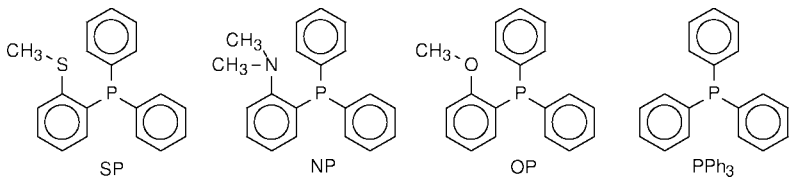
In a typical experiment the reactor was charged with $Rh(NO_3)_3$ (9.0 mg, Fluka), substrate ((4-vinyl-1-cyclohexene 2.5 g, Fluka, >98%), dicyclopentadiene (2.5 g, Aldrich, >95%) or *cis*-1,2,3,6-tetrahydrophthalic anhydride (1 g, Fluka, ∼95%)) and the respective phosphine. In experiments with *cis*-1,2,3,6-tetrahydrophthalic anhydride, ethyl acetate (2.5 g, Prolabo, >99.5%) was added as solvent. The ligand to rhodium ratio was 4 : 1 if not otherwise stated. The system was first flushed with nitrogen and heated to the reaction temperature (90 °C for 4-vinyl-1-cyclohexene, 90 °C for dicyclopentadiene and 150 °C for *cis*-1,2,3,6-tetrahydrophthalic anhydride) with a water/oil bath with continuous stirring, and then pressurised to reaction pressure (20 bar for 4-vinyl-1-cyclohexene, 20 bar for dicyclopentadiene and 12 bar for *cis*-1,2,3,6-tetrahydrophthalic anhydride) with a 1 : 1 molar ratio of H_2 and CO. After 4 h the reaction was stopped by rapid cooling with ice. The reactor was depressurised and a sample was taken for analysis.

The products were analysed with a Hewlett–Packard 5890 GC equipped with a capillary column (HP-1, 60 m × 0.32 mm × 1.0 μm or HP Chiral-β, 30 m × 0.32 mm × 0.25 μm) and a flame-ionisation detector. In addition, the formed aldehydes were identified by GC-MS analysis, and after fractional distillation by ^{1}H NMR spectroscopy.

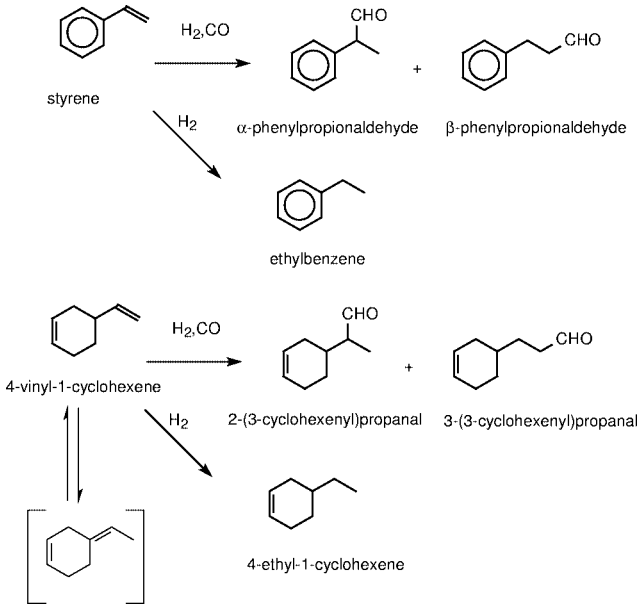
Conversion, selectivity and i/n ratio were calculated on molar basis. Conversion is calculated with respect to the substrate. The i/n ratio of the products is defined as the amount of branched product divided by the amount of linear product.

3. Results

The geometry of styrene and 4-vinyl-1-cyclohexene is fairly similar (scheme 3), but the functionality differs markedly. For example, styrene contains an aromatic ring and a conjugated double bond, so that double-bond isomerisation is not possible; isomerisation can occur in the



Scheme 2. Ligands used in the hydroformylation tests.



Scheme 3. Hydroformylation of styrene and 4-vinyl-1-cyclohexene.

Table 1
Effect of ligand on the hydroformylation of styrene.[a]

Ligand	Conversion (%)	$S_{\text{hydrog.}}$ (%)	S_α (%)	S_β (%)	i/n ratio
SP	16	0	92	8	11.5
NP	8	0	48	52	0.9
OP	n.r.	n.a.	n.a.	n.a.	n.a.
PPh_3[b]	65	0	85	15	5.6
No ligand[c]	35	0	47	53	0.9

[a] 80 °C, 20 bar, L/Rh = 4, styrene/Rh = 3200, 3 h.
[b] L/Rh = 5, styrene/Rh = 2400.
[c] Styrene/Rh = 2400.

Table 2
Effect of ligand on the hydroformylation of 4-vinyl-1-cyclohexene.[a]

Ligand	Conversion (%)	S_{isomer} (%)	S_i (%)	S_n (%)	i/n ratio
SP	~1	n.a.	n.a.	n.a.	n.a.
NP	53	89	2	9	0.2
OP	42	88	2	10	0.2
PPh_3	73	76	4	20	0.2
No ligand	44	90	1	9	0.1

[a] 90 °C, 20 bar, L/Rh = 4, 4-vinyl-1-cyclohexene/Rh = 800, 4 h.

case of 4-vinyl-1-cyclohexene, however. Thus, comparison of these substrates should give some indication of how the functionality of the substrate is reflected in the rate and course of the reaction with a particular catalyst. With both substrates the PPh_3-modified catalyst gave the best conversion (tables 1 and 2). In the case of styrene the regioselectivity of the reaction was constant during the experiment except for the NP-modified catalyst where the selectivity to the branched product deteriorated with time (figure 1). As table 1 shows, the reaction of styrene is highly chemoselective to hydroformylation, and with the SP- and PPh_3-modified catalysts also highly regioselective,

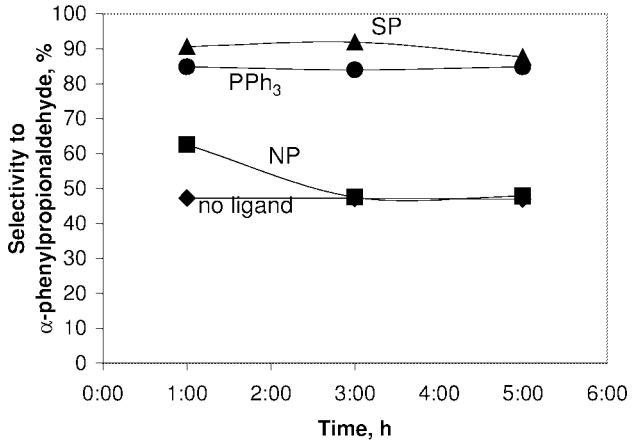
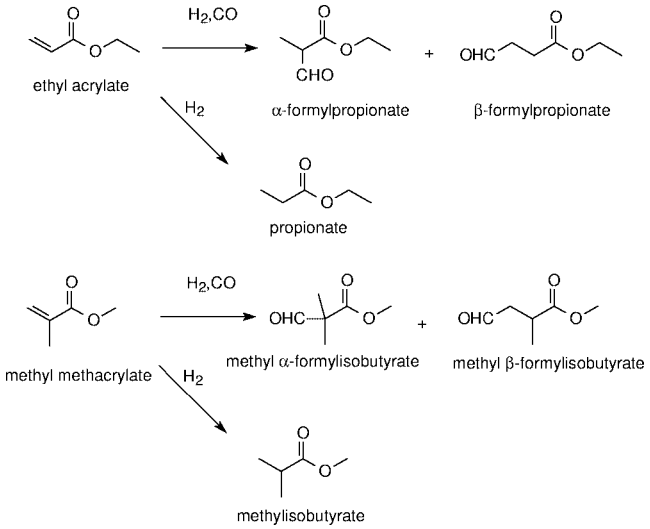


Figure 1. Selectivity to α-phenylpropionaldehyde as a function of time in styrene hydroformylation.



Scheme 4. Hydroformylation of ethyl acrylate and methyl methacrylate.

favouring the formation of the branched aldehyde. The unmodified and NP-modified catalysts lacked regioselective control, giving roughly equal amounts of the two aldehydes, whereas OP-modified catalyst gave no reaction. The chemoselectivity to hydroformylation was rather poor with 4-vinyl-1-cyclohexene, even though no hydrogenation was observed, because isomerisation occurred to a large extent with all the active catalysts. Moreover, all the catalysts showed similar regioselectivity, which in addition did not differ from that of the unmodified catalyst (i/n 0.1–0.2). In contrast to styrene where there was no conversion, the OP-modified catalyst gave moderate conversion of 4-vinyl-1-cyclohexene. The SP-modified catalyst suppressed the reaction in the case of 4-vinyl-1-cyclohexene.

The hydroformylation of ethyl acrylate and methyl methacrylate (MMA) (scheme 4) yields three primary products: α- and β-aldehydes and the respective ester. Structurally and functionally, ethyl acrylate and MMA are very similar and the hydroformylation should proceed analogically. However, the α-carbon in MMA contains an additional methyl group, which could lead to more favoured

Table 3
Effect of ligand on the hydroformylation of ethyl acrylate and methyl methacrylate.[a]

Ligand	Substrate	Conversion (%)	$S_{\text{hydrog.}}$ (%)	$S_{\alpha\text{-ald.}}$ (%)	$S_{\beta\text{-ald.}}$ (%)	i/n ratio
SP	Ethyl acrylate	15	14	82	3	27
SP	Methyl methacrylate	34	7	88	3	28
NP	Ethyl acrylate	5	51	36	13	3
NP	Methyl methacrylate	51	5	58	35	2
OP	Ethyl acrylate	n.r.	n.a.	n.a.	n.a.	n.a.
OP	Methyl methacrylate	n.r.	n.a.	n.a.	n.a.	n.a.
PPh_3	Ethyl acrylate	67	15	74	11	7
PPh_3	Methyl methacrylate	78	2	68	29	2
No ligand	Ethyl acrylate	39	23	23	54	0.4
No ligand	Methyl methacrylate	80	3	14	83	0.2

[a] 100 °C, 60 bar, L/Rh = 4, substrate/Rh = 2500, 3 h.

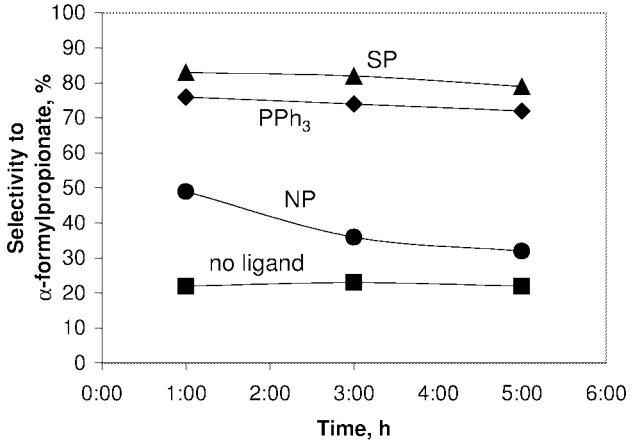


Figure 2. Selectivity to α-formylpropionate as a function of time in ethyl acrylate hydroformylation.

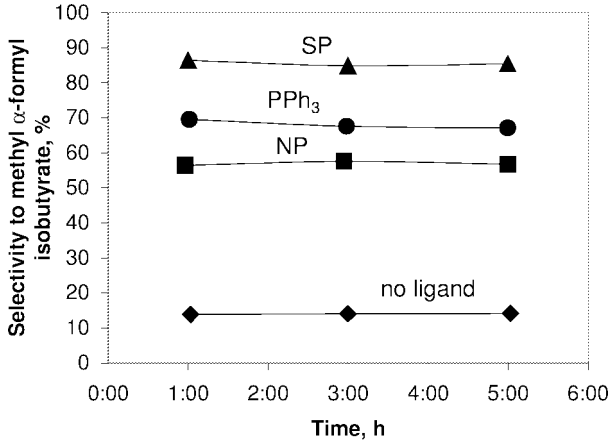


Figure 3. Selectivity to methyl-α-formylisobutyrate as a function of time in MMA hydroformylation.

β-isomer formation relative to ethyl acrylate. Results of the ethyl acrylate and MMA hydroformylation are summarised in table 3. As can be seen, the rate and product distribution were strongly dependent on the catalyst. Conversion was consistently better for MMA than for ethyl acrylate. Likewise, the chemoselectivity, that is the selectivity to aldehydes, was better for MMA. The regioselectivities (i/n ratio) of the individual catalysts were more or less the same for the two substrates, but with the NP- and PPh_3-modified catalysts the i/n ratio of MMA was lower than that of ethyl acrylate; hence, the methyl group on the α-carbon increased the β-aldehyde formation. The SP-modified rhodium catalyst provided regioselective control to α-formylpropionate and methyl-α-formylisobutyrate (i/n 27 and 28, respectively), whereas the unmodified rhodium catalyst gave the highest regioselectivity to β-aldehydes. The NP-modified rhodium catalyst showed exceptionally high hydrogenation activity in the case of ethyl acrylate. In agreement with our previous findings [11], the OP-modified rhodium catalyst gave no reaction with either ethyl acrylate or MMA. Figures 2 and 3 show that the regioselectivities stayed fairly constant during the reaction with all catalysts and with both substrates except for the NP-modified catalyst in the case of ethyl acrylate where the selectivity to branched aldehyde deteriorated with time as with styrene.

Table 4
Effect of ligand on the hydroformylation of dicyclopentadiene.[a]

Ligand	Conversion (%)	$S_{\text{monoald.}}$ (%)	$S_{\text{diald.}}$ (%)	S_{epoxide} (%)	S_{others} (%)
SP	7	86	0	10	4
NP	~1	n.a.	n.a.	n.a.	n.a.
OP	23	91	0	2	6
PPh_3	100	84	13	1	2
No ligand	~1	n.a.	n.a.	n.a.	n.a.

[a] 90 °C, 20 bar, L/Rh = 4, dicyclopentadiene/Rh = 700, 4 h.

The hydroformylation of (functional) terminal alkenes is fairly straightforward. In contrast, published literature on the hydroformylation of cyclic alkenes, particularly dicyclopentadiene [12,13] and *cis*-1,2,3,6-tetrahydrophthalic anhydride [14,15], is scant. Moreover, the reactivity of cyclic alkenes is lower and the reactions are less selective when compared to the terminal alkenes. Hence, the hydroformylation of cyclic alkenes is the ultimate test in assessing the regioselective control of a catalyst. Table 4 shows the results of dicyclopentadiene hydroformylation. Under the testing conditions the hydroformylation occurs selectively in the norbornenyl ring, which is more reactive than the cyclopentadiene ring [13]. The reaction modified with PPh_3 proceeded rapidly, giving the best conversion, but also a

complex mixture of mono- and dialdehydes and epoxides. SP- and OP-modified rhodium catalysts gave low to moderate conversions (7 and 23%, respectively) and formed fairly selectively monoaldehyde. However, it is hard to know whether the selective formation of the monoaldehyde was caused by regioselective control induced by the catalyst or by the extent of the reaction. Surprisingly, NP-modified catalyst gave virtually no conversion.

Laï and Ucciani [7] showed that the distribution of isomeric aldehydes depends, among other things, on the presence of ester groups in the substrate and on the location of these substituents in relation to the reactive double bond. Because ethyl acrylate and MMA induced clear regiocontrol we wished to test whether an ester group in a non-conjugated position relative to the reactive double bond in the molecule could induce a similar effect. The hydroformylation of *cis*-1,2,3,6-tetrahydrophthalic anhydride has only been reported twice [14,15]. Unfortunately, we detected no hydroformylation in our experiments; instead, all the catalysts showed high activity to hydrogenation. GC-MS analysis of the reaction mixture showed the respective triphenylphosphine oxides in the reaction mixture. Possibly the solvent, ethyl acetate (also used in one of the literature methods [15]), oxidised the ligands so that in every case the catalytic activity was mainly due to the unmodified rhodium catalyst.

4. Discussion

4.1. Activity

The hydroformylation activity seems to depend mainly on the modifying ligand. Table 5 summarises the activities obtained in hydroformylation of the substrates with the five catalysts. The activity of the heterodonor-ligand-modified catalysts was lower than that of the PPh_3-modified catalyst with all substrates. The PPh_3-modified catalyst was also the only one that gave reaction with all the substrates. The difference in activity could be due to steric hindrance caused by the heterodonor group in close proximity to rhodium, or to the lower reactivity of phosphorus atom (^{31}P-NMR shifts of PPh_3, NP, SP and OP are -3.3, -12.5, -12.9 and -15.6, respectively). Among the heterodonor-ligand-modified catalysts the OP-ligand-modified catalyst exhibited the most interesting activity behaviour: it was active with 4-vinyl-1-cyclohexene and dicyclopentadiene but did not yield a reaction with styrene or the α,β-unsaturated esters. Suomalainen et al. [16] studied the coordination abilities of these same ligands in reactions with $Rh_2(CO)_4Cl_2$ and $Rh(NO_3)_3$ under various reaction conditions. They found that SP and NP ligands yield mononuclear chelate complexes, while two OP ligands were found to coordinate solely in a monodentate fashion via phosphorus to rhodium, in the same manner as PPh_3. On the basis of the results in table 5 it seems that OP ligand yields a reaction only with non-polar substrates. Possibly, the spatial arrangement of the methoxy groups in *ortho* position differs, depending on the polarity of the substrates, thus enabling the reaction in non-polar media.

Table 5
Hydroformylation activity of the catalysts with tested substrates.

Substrate	SP	NP	OP	PPh_3	No ligand
4-vinyl-1-cyclohexene	–[a]	+[b]	+	++[c]	+
Dicyclopentadiene	+	−	+	++	−
Styrene	+	+	−	++	+
Ethyl acrylate	+	+	−	++	+
Methyl methacrylate	+	++	−	++	++

[a] – no reaction.
[b] + active.
[c] ++ highly active.

4.2. Regioselectivity

Two factors affect the regioselectivity: the substrate and the modifying ligand. Table 6 summarises the regioselectivities (i/n ratios) obtained with the particular catalyst substrate combinations. As can be seen, in the case of 4-vinyl-1-cyclohexene the choice of ligand has no effect on the regioselectivity of the reaction, whereas in the case of α,β-unsaturated esters and styrene, regioselectivity is clearly dependent on the catalyst. Thus, even though the heterodonor ligands exhibit strong individual hydroformylation characteristics, the substrate (i.e., the structure and the functionality of the alkene) has a more pronounced influence on the regioselectivity than does the ligand.

Unsaturated esters and vinyl aromatic derivatives like styrene behave differently from α-alkenes [17], often more easily favouring the formation of branched aldehyde [18, 19]. However, clear regiocontrol (i/n 12–28) with these substrates was only observed for SP-modified catalyst. In fact, in the case of styrene, the NP-modified catalyst even favoured the formation of 3-phenylpropanal, even though formation of 2-phenylpropanal was expected [18]. Structurally the SP and NP ligands do not differ markedly. Moreover, the coordination studies [16] show that they both form a chelate complex with rhodium. However, the NP chelate complex is considered to be weaker than that of SP, possibly because of the lone electron pair of nitrogen. Horner and Simmons [20] proposed that the NP ligand could possess hemilabile character, being able to act as both bidentate and monodentate ligand during the catalysis. Hence, it seems that a strong chelate complex induces regioselective control to α-aldehyde in the case of α,β-unsaturated esters and

Table 6
i/n ratios for the catalysts with tested substrates.

Substrate	SP	NP	OP	PPh_3	No ligand
4-vinyl-1-cyclohexene	n.a.[a]	0.2	0.2	0.2	0.1
Dicyclopentadiene	n.a.	n.a.	n.a.	n.a.	n.a.
Styrene	12	0.9	n.a.	6	0.9
Ethyl acrylate	27	3	n.a.	7	0.4
Methyl methacrylate	28	2	n.a.	2	0.2

[a] n.a. = not applicable.

styrene. Indeed, Tanaka et al. [21] also noted in their studies with α,β-unsaturated esters that any factors weakening the coordination of diphosphines as bidentate ligands were harmful to the branched selectivity.

In addition to the steric factors, the substrates differ in the properties of their double bonds (conjugation and polarity), and thus in their ability to coordinate to rhodium. From the results it would seem that, in addition to the steric factors of the substrate and the properties of the ligand, substrates differing in the properties of their reactive double bond could induce a different type of reactivity in a particular catalyst according to the individual fluctuating behaviour of the ligand. Thus, in the case of SP-ligand-modified reaction and α,β-unsaturated esters or styrene, the regioselective control is obtained through synergy between the substrate and the catalyst.

5. Conclusions

Systematic variation of the heterodonor atom in the *ortho* position of the ligand showed that the heterodonor atom has a significant influence on the activities and selectivities of the reaction. Activity is mainly influenced by the modifying ligand, whereas regioselectivity is more influenced by the substrate. Additional to the steric factors of the substrate the properties (conjugation and polarity) of the reactive double bond play a role so that the regioselectivity of hydroformylation seems to depend on the synergy between the substrate and the catalyst. Clear regiocontrol was obtained with SP-modified catalyst and α,β-unsaturated esters or styrene.

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