Hydroformylation of methyl methacrylate with heterodonor phosphinerhodium catalysts prepared *in situ*

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The catalytic activity and selectivity of heterodonor phosphinerhodium catalysts prepared *in situ* were tested in the hydroformylation of methyl methacrylate at 100 °C and 60 bar. Systematic variation of the heterodonor atom in the *ortho* position of the ligand showed that the heterodonor atom has a significant influence on the initial reaction rates and selectivities of the reaction. An exceptionally high selectivity to methyl-α-formylisobutyrate was observed with [*o*-(methylthio)phenyl]diphenylphosphine ligand, which gave a branched to normal ratio of about 27. Study was also made of the product distribution during the experiment. The decrease in the branched to normal ratio was more severe with the diphosphine ligands than with the other heterodonor ligands.

Keywords: bidentate heterodonor ligands, methyl methacrylate, hydroformylation

1. Introduction

One of the major industrial applications for homogeneous transition metal catalysts is hydroformylation, which offers powerful routes for preparing a wide variety of significant intermediates, most notably for the pharmaceutical, cosmetics, adhesives, and coating industries [1–3]. A key issue in hydroformylation is how to control the ratio of linear to branched products. The challenge in ligand design is, thus, to understand the factors that lead to a certain product distribution and to apply this knowledge in ligand development.

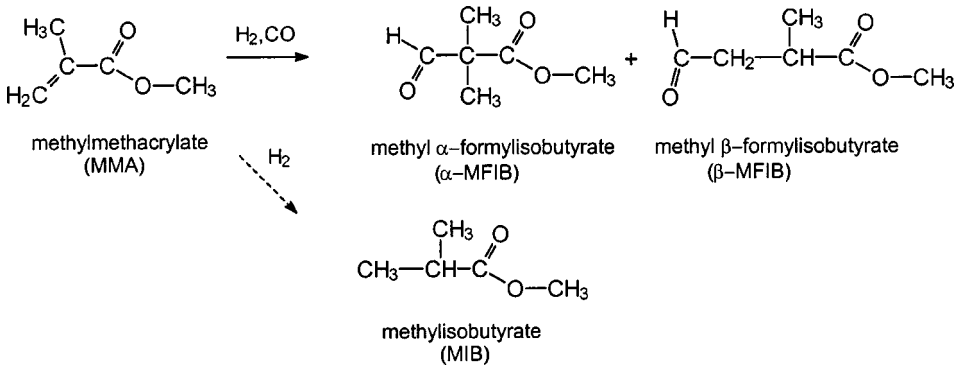
Phosphines and their coordination chemistry have been studied extensively. Newly designed and synthesised polydentate ligands are now being used, for example in five-coordination complex chemistry [4–7] and homogeneous catalysis [8–14]. Chelating phosphines have proved especially useful in modifying the electronic and steric properties of reactive metal centres, offering considerable advantages in the design of new homogeneous catalysts.

Under hydroformylation conditions, methyl methacrylate (MMA) is mainly converted into branched methyl-α-formylisobutyrate (α-MFIB) or the linear isomer, methyl-β-formylisobutyrate (β-MFIB). Hydrogenation also occurs to some extent yielding methyl isobutyrate (MIB) (scheme 1). Hydroformylation of MMA with a catalyst prepared *in situ* from $Rh(NO_3)_3$ and phosphines takes place in toluene solution almost independently of temperature and pressure. The branched to normal selectivity is highly dependent on the reaction conditions, however [15,16]. In the case of α,β-unsaturated esters, elevated pressure and low-temperature favour the formation of the α-isomer, whereas the opposite of the trend is observed for β-isomer. Ligand to rhodium ratios below four favour the formation of β-MFIB, whereas the ratios equal to or higher than four enhance the formation of α-MFIB. High selectivity towards β-MFIB can easily be obtained with almost any ligand at sufficiently low pressures and high temperatures; thus, the challenge in ligand development is to achieve high selectivity towards α-MFIB.

During the late 70's Tanaka et al. [15] studied the hydroformylation of MMA with $Rh_2Cl_2(CO)_4$ and linear unsubstituted diphosphine ligands. Later, triphenyl phosphine, the most used ligand in industrial processes, and its various derivatives were studied as possible ligand alternatives [16,17]. Recently, Alper and Zhou [18] introduced a zwitterionic rhodium 1,4-bis(diphenylphosphino)butane complex with high α-selectivity. However, problems have been encountered with all these ligands, including low reactivity, poor regioselective control and the extreme dependence of regioselectivity on process variables.

In general, PR_3 type ligands work to stabilise the catalyst. In addition, chelating and bidentate ligands contribute to the catalytic activity and selectivity [10]. Bidentate phosphorus–nitrogen ligands are expected to be useful in homogeneous catalysis since the nitrogen can usually be displaced by ligands such as CO and olefins, thus making the coordination site readily available [9]. Methoxy and dimethylaniline substituents in the *ortho* position of phenyl groups are known to induce high optical activity to derivatives of α-acylaminoacrylic acid in homogeneous hydrogenation with Rh(I)–phosphine complexes [19].

We anticipated that the use of potentially bidentate [*o*-(methoxy)phenyl]diphenylphosphine, [*o*-(N,N-dimethylamino)phenyl]diphenylphosphine, [*o*-(methylthio)phenyl] diphenylphosphine and 1,2-bis[bis(2-methylthiophenyl) phosphino]ethane ligands might lead to steric control similar to that obtained with diphosphines. Systematic vari-



Scheme 1. Hydroformylation products of methyl methacrylate.

ation of the heterodonor atom was accordingly carried out to modify the electronic and steric properties of the *in situ* formed catalysts. The behaviour of the different *in situ* formed *ortho*-substituted heterodonor phosphine rhodium catalysts was then studied in the hydroformylation of MMA. The catalytic activity and selectivity of plain rhodium nitrate and the *in situ* formed triphenyl phosphine rhodium nitrate catalyst were recorded in order to serve as references.

2. Experimental

The ligands used in the experiments are shown in scheme 2. The commercial ligands were triphenylphosphine (PPh_3, Fluka, 99%), 1,2-bis(diphenylphosphino) ethane (DPPE, Fluka, 98%) and 1,4-bis(diphenylphosphino) butane (DPPB, Fluka, >97%). The synthesis of the ligands [*o*-(methylthio)phenyl]diphenylphosphine (SP), [*o*-(methoxy)phenyl]diphenylphosphine (OP), [*o*-(N,N-dimethylamino)phenyl]diphenylphosphine (NP) and 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane (DSPPE) is described below. Commercially available reagents were used without further purification if not otherwise stated. Solvents were dried and degassed before use. All the ligand syntheses were carried out in argon atmosphere with use of Schlenk techniques.

2.1. Ligand synthesis

NMR spectra were recorded on Bruker AM200 and Bruker DPX400 spectrometers. Spectra were recorded in the solvent indicated, locked on solvent deuterium and referenced to residual solvent protons. In ^{1}H spectra TMS was used as an internal reference and in ^{31}P spectra 85% H_3PO_4 was used as an external reference. Elemental analyses were done with a Perkin–Elmer 2400 Series II CHNS/O Analyzer.

2.1.1. [o-(methylthio)phenyl]diphenylphosphine (SP) [20]

o-bromothioanisole (Aldrich, 97%) was lithiated with n-butyllithium (Aldrich, 2.5 M solution in hexane) at 0 °C in diethyl ether. The mixture was stirred for 1 h at 0 °C, after which diphenylchlorophosphine (Fluka, 97%) was added in diethyl ether. The mixture was stirred at 0 °C for one more hour. The white precipitate was hydrolysed with 0.2 M hydrochloric acid, collected on a filter and washed with water, ethanol and diethyl ether. The product was dried in vacuum. Yield 48.6%. Found: C 73.5, H 5.6, S 10.6%. Calcd. for $C_{19}H_{17}PS$: C 74.0, H 5.6, S 10.4%. ^{1}H-NMR δ 7.33 (m, phenyl), 7.05 (k, thioanisole), 6.76 (q, thioanisole) and 2.43 ppm (s, methyl). ^{31}P{^{1}H}-NMR δ −18.09 ppm (s).

2.1.2. [o-(methoxy)phenyl]diphenylphosphine (OP)

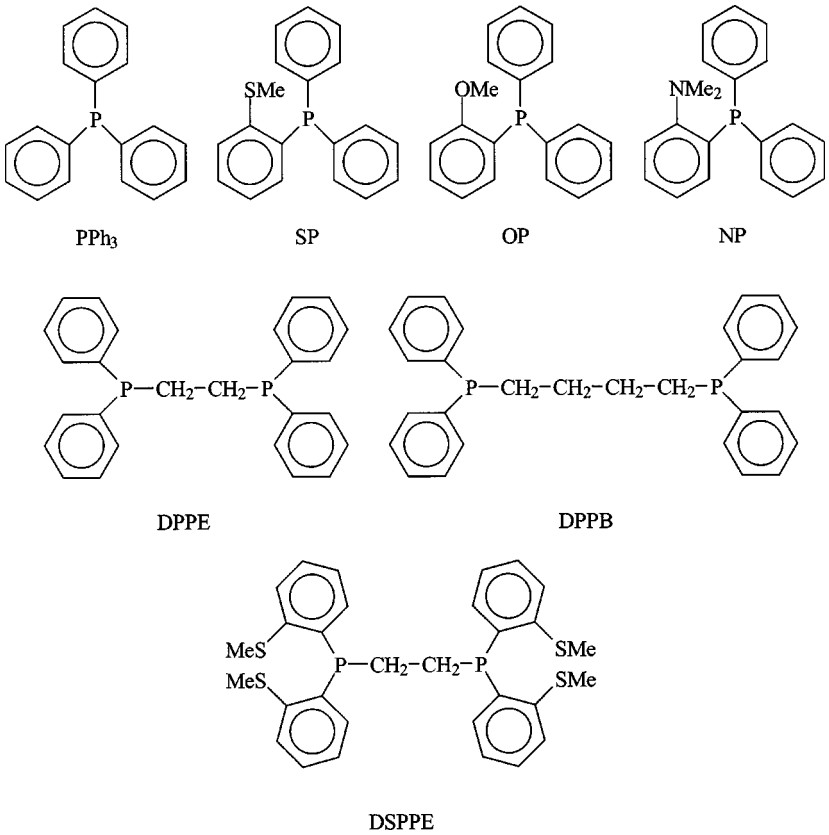
[*o*-(methoxy)phenyl]diphenylphosphine was prepared according to the method for SP from o-bromoanisole (Aldrich, 97%), n-butyllithium and diphenylchlorophosphine in diethyl ether. The mixture was stirred at 0 °C for 30 min and at room temperature for 30 min before hydrolysation. Yield 56.1%. Found: C 76.3, H 5.9%. Calcd. for $C_{19}H_{17}OP$: C 78.1, H 5.9%. ^{1}H-NMR δ 7.33 (m, phenyl), 6.87 (q, anisole), 6.67 (t, anisole) and 3.75 ppm (s, methyl). ^{31}P{^{1}H}-NMR δ −15.64 ppm (s).

2.1.3. [o-(N,N-dimethylamino)phenyl]diphenylphosphine (NP) [21]

A mixture of N,N-dimethylaniline (EGA, 99%), hexane and n-butyllithium was refluxed for 5 h. Diphenylchlorophosphine was added to the reaction mixture at −10 °C in hexane. After refluxing of the reaction mixture for five more hours, deoxygenated water was added. The organic layer was separated and concentrated in vacuum. On cooling to −20 °C, the product was precipitated. Yield 12.4%. Found: C 78.5, H 6.6, N 4.3%. Calcd. for $C_{20}H_{20}NP$: C 78.7, H 6.6, N 4.6%. ^{1}H-NMR δ 7.31 (m, phenyl), 7.00 (t, aniline), 6.78 (dd, aniline) and 2.60 ppm (s, methyl). ^{31}P{^{1}H}-NMR δ −12.50 ppm (s).

2.1.4. 1,2-bis[bis(2-methylthiophenyl)phosphino]ethane (DSPPE) [22]

Liquid o-bromothioanisole (Aldrich, 97%) in diethyl ether was treated dropwise with n-butyllithium at 0 °C. The solution was stirred for 1 h, after which 1,2-bis(dichlorophosphino)ethane (Aldrich, 97%) was added slowly. The resulting yellow precipitate was hydrolysed with 0.2 M hydrochloric acid. After 20 min stirring the white precipitate was filtered and washed with small amounts of



Scheme 2. Ligands used in the hydroformylation experiments.

water and diethyl ether. The product was dried in vacuum and recrystallised from dichloromethane. Yield 69.9%. Found: C 61.37, H 5.40%. Calcd. for $C_{30}H_{32}S_4P_2$: C 61.83, H 5.53%. ^{1}H-NMR δ 7.29 (m, thioanisole), 7.04 (m, thioanisole), 2.42 (s, methyl) and 2.18 ppm (t, ethyl). ^{31}P{H}-NMR δ −30.13 ppm (s).

2.2. Hydroformylation procedure

All the hydroformylation experiments were carried out in a 250 ml autoclave (Berghof) equipped with a sampling system. The experiments were carried out in semi-batch mode. A disposable inner Teflon reactor 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 autoclave was charged with $Rh(NO_3)_3$ (6.5 mg, Fluka), methyl methacrylate (5 g, Merck, >99%), toluene (25 g, Fisher Scientific International, >99%), internal standards decane (1 g, Fluka, >98%) and cyclohexane (1 g, Riedel de Häen, >99%), and triphenylphosphine (20.8 mg). In every case the ligand to rhodium ratio was 4 : 1. The system was first flushed with nitrogen and heated to 100 °C with continuous stirring, and then pressurised to 60 bar 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.

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

Calculations of conversion, selectivity, yield and i/n ratio were based on moles. Conversion was calculated with respect to MMA. The i/n ratio of the products was defined as the amount of branched product divided by the amount of linear product. The initial formation rates were calculated according to the equation

$$r_{\text{initial}} = \frac{n_{\text{tot}}}{m_{\text{mixture}}} \frac{\mathrm{d}X_i}{\mathrm{d}t}, \tag{1}$$

in which i is either α- or β-MFIB and $\mathrm{d}X_i/\mathrm{d}t$ is calculated by fitting a third-order polynomial function to a curve presenting conversion as a function of time and then calculating the derivative of the polynomial function at 20 min.

3. Results and discussion

The ligands had significantly different effects on the conversions and yields of α- and β-MFIB, whereas the formation of the by-product MIB was virtually the same with all ligands. The addition of PPh_3 ligand had no influence on the conversion level (after 5 h: plain $Rh(NO_3)_3$ 89%,

with PPh_3 88%) whereas the addition of ligands SP, NP, DPPE and DPPB decreased it noticeably (44, 65, 31 and 54%, respectively). The addition of OP and DSPPE gave no reaction. Lee and Alper [23] found that the addition of DPPB inhibited the reaction in MMA hydroformylation and concluded that the decrease in conversion was specific for that substrate, since no decrease occurred with other α,β-unsaturated esters. However, a similar decrease in conversion has been noticed in the hydrogenation of 1-hexene with *ortho*-substituted phenyl phosphines [8]. Thus, the steric effects of the ligands must play an important role.

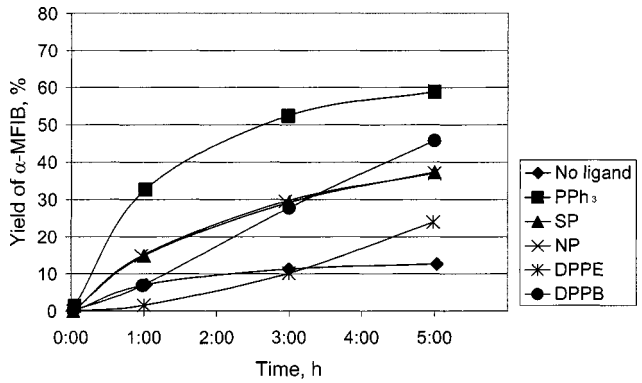


Figure 1. Yield of α-MFIB as a function of time. Ligands OP and DSPPE gave no reaction (100 °C, 60 bar, MMA/Rh = 2500, L/Rh = 4).

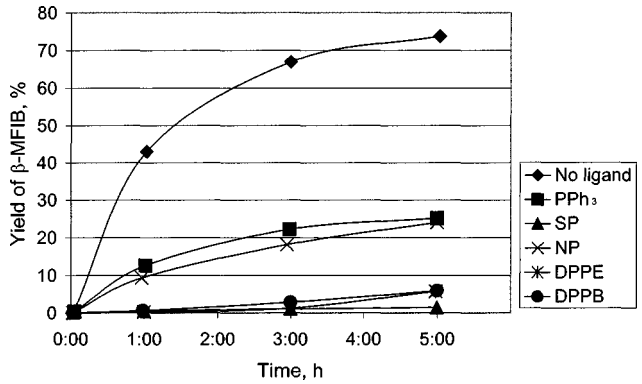


Figure 2. Yield of β-MFIB as a function of time. Ligands OP and DSPPE gave no reaction (100 °C, 60 bar, MMA/Rh = 2500, L/Rh = 4).

Comparison of the product formation as a function of time revealed clear differences in the behaviour of the ligands (figures 1 and 2). With triphenylphospine-based ligands as with $Rh(NO_3)_3$, the reaction started rapidly and then slowed down, reaching a maximum yield, but in the case of the diphosphine ligands the beginning of the reaction was extremely slow and the rate of the reaction accelerated only after 1 h.

To further clarify the qualitatively observed variations in the activity of the different ligands, initial formation rates were calculated for α- and β-MFIB (table 1). Comparison of the performance of different ligands revealed that, even though PPh_3 gave the best initial formation rate of α-MFIB, the best overall result was obtained with the SP ligand since it produced practically no β-isomer. Interestingly, SP and NP gave exactly the same initial formation rate of α-MFIB, but the initial formation rates of β-MFIB differed markedly.

Figure 3 shows that the ligand has a profound effect on the selectivity in MMA hydroformylation. As expected, the addition of PPh_3 favoured the formation of α-isomer, but

Table 1
Initial formation rates for α- and β-MFIB with various ligands.[a]

Ligand	Initial formation rate ($\times 10^{-6}$ mol/$g_{mixture}$ min^{-1})	
	α-MFIB	β-MFIB
–	2.4	14.0
PPh_3	11.0	4.2
SP	5.2	0.2
OP	n.r.[b]	n.r.
NP	5.4	3.4
DPPE	0.6	0.06
DDPB	2.4	0.2
DSPPE	n.r.	n.r.

[a] Reaction conditions 100 °C, $H_2:CO$ = 1:1, MMA/Rh = 2500, L/Rh = 4.
[b] n.r. = no reaction.

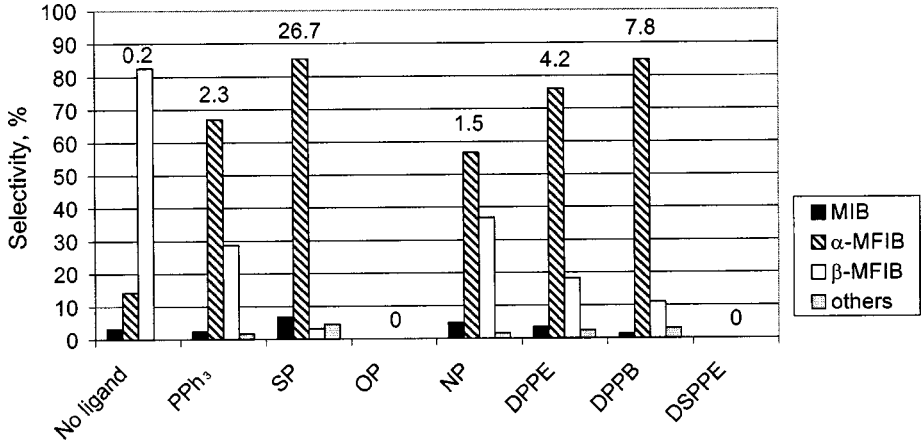


Figure 3. Selectivities of different ligands in MMA hydroformylation. The numbers on top of the pillars represent branched to normal ratio of the products (100 °C, 60 bar, MMA/Rh = 2500, L/Rh = 4, reaction time 5 h).

the selectivity to this isomer nevertheless remained poor. The selectivity obtained with the NP ligand was similar to that with PPh_3; the SP ligand yielded almost totally only α-MFIB (85%) and the OP ligand gave no reaction. Thus, the effect of the heterodonor phospine ligands NP, SP and OP was very different, even though the steric structure of the ligands did not differ appreciably. The decrease in the branched to linear ratio with respect to time was, after 5 h, approximately 10% with PPh_3, SP and NP (figure 4). With plain rhodium nitrate, no change occurred, the i/n ratio being 0.2 during the entire run. It is worth noting that according to preliminary calculations, in which the required thermodynamical properties of α-MFIB and β-MFIB were estimated by the methods of Joback [24], the thermodynamical i/n ratio is below 0.1. This means that the high selectivity to α-MFIB is due to the initial mechanism of the reaction and not to the isomerisation of β-MFIB to α-MFIB.

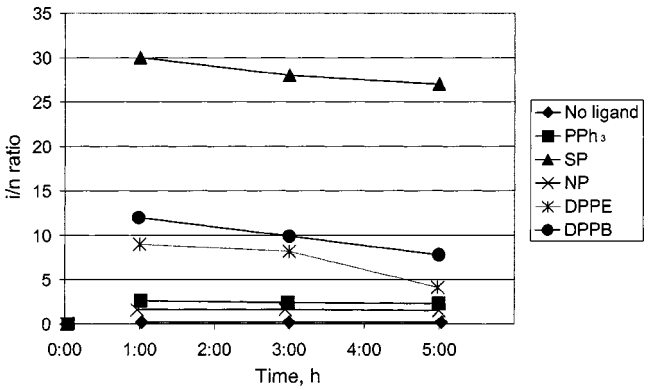


Figure 4. i/n ratio as a function of time (100 °C, 60 bar, MMA/Rh = 2500, L/Rh = 4).

Increase in pressure led to enhanced initial formation rates. For example the initial formation rate of α-MFIB increased with the SP ligand from 1.0×10^{-6} to 5.2×10^{-6} mol/$g_{mixture}$ min^{-1} and with PPh_3 from 2.4×10^{-6} to 11.0×10^{-6} as the total pressure was increased from 20 to 60 bar. Table 2 shows the effect of pressure on α-MFIB selectivity with different ligands. The α-MFIB selectivity increased with increasing pressure with plain rhodium nitrate as well as with the NP and OP ligands. The literature results obtained with the S,S-Chiralphos [1], PPh_3 [16,17], PBu_3 [17] ligands and PPh_3 bound to styrene-divinylbenzene resin [16] also obeyed this trend. The only exception was the SP ligand as the α-selectivity stayed constant regardless of the pressure. Moreover, the SP ligand exhibited a significantly high α-selectivity (86%) already at 20 bar when compared to that of the other tested ligands. The α-selectivities obtained with the PPh_3 ligand by Pittman et al. [16] and Prókai et al. [17] are higher than what we obtained with the same ligand. The results are not, however, fully comparable due to differences in reaction conditions, rhodium precursor and reaction time.

According to Horner and Simons [8], the binding tendency for rhodium increases in the order OMe, NMe_2, SMe. From the results obtained with the NP and SP ligands it would appear that the α-selectivity increases with the increasing binding tendency of the substituent group in *ortho* position. However, the OP ligand suppressed the hydroformylation activity of rhodium totally. This could be explained by the formation of an extremely strong complex with rhodium and two or even three OP ligands, preventing ligand substitution or displacement steps from taking place in the catalytic cycle. This is in partial contradiction with the literature, however, where it has been postulated that

Table 2
Effect of pressure on α-MFIB selectivity.[a]

Ligand	α-MFIB selectivity (%)				Ref.
	20 bar	40 bar	60 bar	80 bar	
No ligand	4	–	14	–	
PPh_3	30	–	67	–	
SP	86	88	85	87	
OP	n.r.[b]	n.r.	n.r.	–	
NP	18	–	57	60	
S,S-Chiralphos[c]	–	69 (50 bar)	–	–	[1]
PPh_3[d]	66 (15 bar)	–		86	[17]
PBu_3[d]	18 (15 bar)	–	–	49	[17]
Styrene-divinylbenzene resin[e]	51 (14 bar)	72 (28 bar)	–	–	[16]
PPh_3[f]	57 (14 bar)	93 (42 bar)	94 (56 bar)	–	[16]

[a] Reaction conditions: 100 °C, H_2 : CO = 1 : 1, MMA/Rh = 2500, L/Rh = 4, reaction time 5 h.
[b] n.r. = no reaction.
[c] Reaction conditions: precursor $[Rh(CO)_2Cl]_2$, 100 °C, H_2 : CO = 1 : 1, MMA/Rh = 2000, L/Rh = 2, reaction time 23 h.
[d] Reaction conditions: precursor $[Rh(NBD)_2Cl]_2$, 100 °C, H_2 : CO = 1 : 1, MMA/Rh = 20, L/Rh = 2, reaction time 3 h.
[e] Reaction conditions: $(P–PPh_2)_3Rh(CO)$, 80 °C, H_2 : CO = 1 : 1, MMA/Rh = 400, L/Rh = 5, reaction time from 21 to 24 h.
[f] Reaction conditions: $RhH(CO)_2PPh_3$, 80 °C, H_2 : CO = 1 : 1, MMA/Rh = 400, L/Rh = 3, reaction time 18, 4 and 8 h, respectively.

OP-type ligands are not able to form stable chelates with rhodium(I) [21].

The NP ligand behaves more like a monodentate phosphine, giving approximately the same kind of product distribution as triphenylphosphine. This would imply that, even if a chelate is formed, the bond between nitrogen and rhodium will dissociate during the catalytic cycle. The high α-selectivity of the SP ligand is probably due to its strong chelating ability and to the stereochemistry of the formed complex. It seems that the steric and electronic properties of the *in situ* formed SP–rhodium complex only allow the formation of α-MFIB.

Clear variations were also observed in the selectivities of the diphosphine ligands. DPPE performed relatively well in regard to both activity and α-selectivity. However, product distributions as well as the conversions were even better with the analogue DPPB even though, according to Tanaka et al. [15], the two ligands should give similar results.

The decrease in the branched to linear ratio after 5 h with DPPE and DPPB was more severe (53 and 35%, respectively) than with other ligands (figure 4). This decrease in i/n ratios represents a deterioration of α-selectivity from 90 to 76% (DPPE) and from 91 to 85% (DPPB). Thus, the experimental results indicate that the rhodium chelates of DPPE and DPPB will not remain in stable form during the catalytic reaction leading to changes in the product distribution during the experiment. A possible explanation is that, because DPPE and DPPB are able to act as either mono- or bidentate ligands [25] as the reaction proceeds the behaviour of the ligands will shift towards monodentate behaviour favouring the formation of β-MFIB. In fact, it has been suggested that any factors weakening the coordination of a diphosphine as a bidentate ligand are harmful to high α-selectivity [15].

DSPPE was chosen as a linear substituted phosphine ligand because of the encouraging results obtained with SP. However, the DSPPE ligand gave no hydroformylation reaction within 5 h. Apparently, the ligand blocked the activity of rhodium by forming an inactive and possibly insoluble complex; for after the reaction the reactor walls were covered with a reddish-yellow residue.

4. Conclusions

We have demonstrated that the heterodonor atom in the *ortho* position of the phenyl ring of the ligand significantly influences the product distribution in MMA hydroformylation. The SP ligand indeed exhibits considerably higher selectivity to α-MFIB than do DPPE and DPPB, which are known to be very effective in the selective α-formylation of α,β-unsaturated esters. Moreover, the i/n ratio of the SP ligand does not decrease significantly during the experiment. In addition, the high α-selectivity is obtained with the SP ligand regardless of the total pressure. These results are promising and work is continuing to evaluate the effect of the substrate as well as the mechanism of the reaction.

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