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# Rhodium catalysed hydroformylation of higher alkenes using amphiphilic ligands

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## Abstract

A variety of amphiphilic ligands has been synthesised comprising  $\text{Ph}_2\text{ArP}$  (Ar = 3-hydroxyphenyl, 4-carboxyphenyl),  $\text{Ph}_n\text{Ar}_{3-n}\text{P}$  (Ar = 4- $\text{PhCH}_2\text{X}$ , X = NEt<sub>2</sub>, NMePh, NPh<sub>2</sub>;  $n = 1-2$ ) and  $\text{Ph}_n\text{Ar}_{3-n}\text{P}$  (Ar = 3/4-pyridyl;  $n = 1-2$ ). In the hydroformylation of oct-1-ene (80°C, 20 bar syngas, toluene) the ligands were shown to be comparable with triphenylphosphine. Turn-over frequencies of  $2.2 \times 10^3$  (mol aldehyde · mol Rh<sup>-1</sup> · h<sup>-1</sup>) were found for most ligands with an oct-1-ene concentration of 0.84 M. The pyridylphosphines were up to two times faster. The selectivity of the hydroformylation is not affected by the modifications and in all cases aldehydes were formed with a n/b ratio of 2.8.  $\text{Ph}_2\text{P}(4\text{-C}_6\text{H}_4\text{COOH})$  showed low catalytic activity under standard conditions. Preliminary experiments have shown that the new ligands in their protonated, water-soluble form do not produce active hydroformylation catalysts.

**Keywords:** Alkenes; Hydroformylation; Phosphine derivatives; Rhodium; Water-soluble triarylphosphines

## 1. Introduction

To date, for industrial use, rhodium is only applied for the hydroformylation of low-boiling alkenes such as propene [1]. Hydroformylation of higher alkenes is still performed with the less active and selective cobalt catalysts. Separation of the high-boiling aldehydes and the catalyst is generally done by distillation or extraction. The vigorous distillation conditions required can result in degradation of the cobalt catalyst with concomitant loss of metal. Since the cobalt catalysts are relatively cheap these processes are still commercially attractive. Commercial application of a faster but also more expensive rhodium catalyst in

the hydroformylation of higher alkenes cannot tolerate a rhodium loss higher than 0.1 ppm in the reaction products [2]. The high boiling points of the products imply that a separation method other than distillation should be applied.

There are two promising methods for the separation of rhodium catalysts and high-boiling products. One approach involves anchoring the homogeneous catalyst to a support such as silica, resins or polymers. Until now, no industrial application has been reported; apparently the penalties for potential drawbacks (complicated synthesis, stability, leaching and selectivity) are too high to be paid.

Another approach comprises the use of water-soluble rhodium complexes which allows an easy separation of the catalyst and the organic reagents.

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To render rhodium catalysts water-soluble, many water-soluble ligands have been prepared and studied for their catalytic properties in the hydrogenation and hydroformylation reaction [3]. Most ligands are phosphines containing functional groups like sulphonate [4], ammonium [5], phosphonium [6], and carboxyl [7] groups. Water-soluble derivatives of chiral phosphines like DIOP and Chiraphos, both cationic [8] and anionic [9] versions, have been reported. Fell et al. used phosphines which are not only water-soluble but also have phase transfer properties [10].

Most of the research done in the field of water-soluble complexes is based on two-phase catalysis, i.e. the system consists of an aqueous phase containing the catalyst and an organic phase containing the reagents, both of which are in contact during the reaction. The main disadvantage of two-phase catalysis is that the reaction rates may be low, primarily due to the low solubility of the substrate in water and/or phase transfer limitations. The rhodium catalysed hydroformylation process [2] of propene using the water-soluble trisulphonated triphenylphosphine (TPPTS) may therefore not be applicable to higher alkenes. The use of quaternary ammonium or phosphonium salts which serve as solubilising agents in water has recently been claimed to overcome these obstacles [11].

A different approach involves the use of an amphiphilic catalyst which is soluble in either an organic or aqueous phase depending on the pH. The homogeneously catalysed reaction is first carried out in the organic phase (or pure substrate). After the hydroformylation water of a certain pH is used to extract the catalyst. The aqueous phase containing the water-soluble catalyst is then neutralised and the catalyst is extracted into a fresh organic phase. The most important advantage of this method is that during the hydroformylation the system is homogeneous with a concomitantly high reaction rate. Ideally, the catalytic complex remains intact. Relatively few reports concerning this subject have appeared until now [12]. This approach is applied for industrial use in the Kuhl-

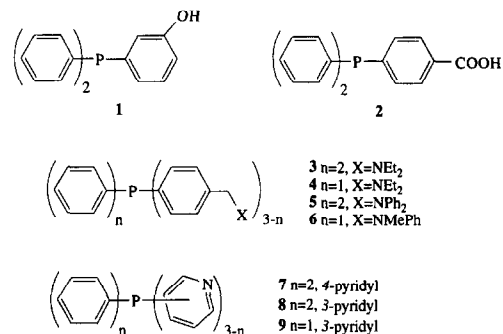


Fig. 1. The amphiphilic ligands.

mann process [1], in which alkenes are hydroformylated using the amphiphilic complex  $\text{HCo}(\text{CO})_4$  as the catalyst. In a recent patent application [13] a different approach worth mentioning has been proposed in which higher alkenes ( $C > 7$ ) are hydroformylated with a hydrido rhodium carbonyl catalyst after which water-soluble nitrogen-bidentate ligands are used as complexing agents to extract the rhodium into an aqueous solution.

As part of the present study we have synthesised a variety of ligands which, when coordinated to rhodium, form complexes having an amphiphilic character. The ligands are based on triphenylphosphine, which industrially is still the most applied ligand. Moreover, its coordination chemistry and catalytic properties are well documented.

The series comprises triphenylphosphines modified with different types of acidic or basic functionalities, which were placed on *meta* or *para* positions in order to minimise steric interactions and to prevent chelation.

The present work describes the syntheses of these ligands and their performance as ligands in the rhodium catalysed hydroformylation of oct-1-ene. Also some preliminary experiments are reported involving two-phase catalysis to investigate the scope of the newly synthesised ligands.

## 2. Results and discussion

### 2.1. Synthesis

The modified triphenylphosphines that have been used are pictured in Fig. 1. Two of these

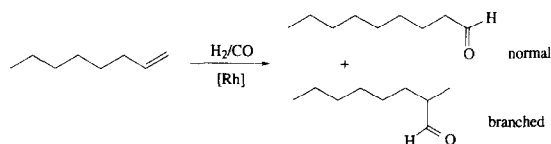


Fig. 2. Hydroformylation of oct-1-ene.

ligands are modified with an acidic functionality. The synthesis of ligand **1** was described by Lamza [14], but a different work-up procedure proved necessary to obtain the pure compound. For the known methoxy precursor [14] a different method was used.

We have synthesised ligand **2**, previously used by Russell [7], following the method described for diphenyl(2-carboxyphenyl)phosphine [15].

The series of ligands **3–6** comprises a group of phosphines containing one or two benzylic amino groups of different basicity. The *N*-4-bromobenzylidiphenylamine compound was synthesised according to the method described by Davidson [16].

Finally, we used the group of pyridylphosphines **7–9**.

## 2.2. Catalysis in general

The ligands have been tested in the rhodium catalysed hydroformylation reaction of oct-1-ene as a representative of a higher alkene. Both the *normal* and the *branched* aldehydes are formed (Fig. 2).

Unmodified triphenylphosphine has been tested under the same hydroformylation conditions as a reference ligand. The active rhodium phosphine complexes, having the general formula  $\text{HRh}(\text{CO})_n(\text{L})_m$ , were formed in situ by pressurising a toluene solution of  $\text{Rh}(\text{acac})(\text{CO})_2$  and a twenty-fold excess of the ligand with syngas. The hydroformylation results using the various ligands are listed in Table 1.

A first important conclusion that can be drawn from Table 1 is that the extra functionalities on the phosphine ligands do not have any influence on the selectivity of the hydroformylation reaction. In all cases, aldehydes are formed with a *n/b* ratio of about 2.8, together with a small per-

centage of isomerised oct-1-ene. No alkane or alcohol formation has been observed. From Table 1 it can also be concluded that all ligands, apart from ligand **2** and the pyridylphosphines **7–9**, show turn-over frequencies comparable with that of triphenylphosphine.

## 2.3. Catalysis with the pyridylphosphines 7–9

From Table 1 it follows that the pyridylphosphines show an increasing trend of TOF values:  $\mathbf{9} > \mathbf{7} \gg \mathbf{8} > \text{PPh}_3$ .

When the hydroformylation was performed with triphenylphosphine in the presence of pyridine no rate increase was observed so the higher rate observed for the pyridylphosphines must be a ligand effect.

The trend suggests a correlation between increasing TOF's and increasing electron-withdrawing groups attached to the phosphorus atom. Ligand **9** incorporates two electron-withdrawing pyridyl rings on the phosphorus atom. Ab initio calculations [17] show that the  $\pi$ -electron density on the *para*-position is lower than on the *meta*-position. Therefore, the *para*-pyridyl ring in ligand **7** is more electron-withdrawing than the *meta*-pyridyl ring in ligand **8**. The effect of one *para*-pyridyl ring almost equals the effect of two *meta*-pyridyl rings.

The trend that ligands with higher  $\chi$  values show higher rates in the hydroformylation reaction has been reported in the literature [18,19]. Furthermore, these reports state that the higher rates were accompanied by higher *n/b* ratios and in one case [19] by an increase in isomerisation. Remarkably, in our case the rates increase – especially when using ligands **7** and **9** – but the *n/b* ratios remain exactly the same. We do find an increase in isomerisation. This is tentatively explained as follows: With a higher  $\chi$  value of the phosphines the rhodium becomes more electrophilic, resulting in a decrease of the  $\pi$ -backbonding to CO. The CO molecules are now less strongly bonded to the rhodium centre and alkene coordination by substituting a CO molecule becomes more facile. It has been found [20] that

Table 1  
Hydroformylation of oct-1-ene

Ligand	Time (min)	Conversion (%) <sup>a</sup>	Selectivity (%)			n/b	TOF ( $\times 10^{-3}$ ) <sup>c</sup>
			isom <sup>b</sup>	n-ald	b-ald		
PPh <sub>3</sub>	10	7.3	1.4	72.6	25.9	2.8	2.2
	60	42.1	1.3	72.7	26.0	2.8	2.1
	120	81.2	1.5	72.6	25.9	2.8	2.0
<b>1</b>	10	7.2	0.8	73.4	25.8	2.8	2.1
	60	38.9	0.9	73.3	26.0	2.8	1.9
	120	76.6	0.8	73.1	26.1	2.8	1.9
<b>2</b>	30	0.5	–	74.3	25.6	2.9	0.05
	70	1.1	–	73.6	26.4	2.8	0.05
<b>3</b>	10	6.7	0.2	72.8	26.8	2.7	2.0
	60	45.2	0.3	72.9	26.8	2.7	2.3
	120	76.2	0.3	73.3	26.0	2.8	1.9
<b>4</b>	10	6.2	0.6	72.7	26.3	2.8	1.9
	60	37.7	0.6	72.7	26.4	2.8	1.9
	120	72.6	0.8	73.0	26.1	2.8	1.8
<b>5</b>	10	8.0	0.4	73.2	26.2	2.8	2.4
	60	45.1	0.2	73.5	26.2	2.8	2.3
	120	83.3	0.3	73.1	26.5	2.8	2.1
<b>6</b>	10	8.3	1.2	72.9	26.1	2.8	2.5
	60	46.3	1.0	73.0	26.0	2.8	2.3
	120	85.0	1.2	72.8	26.0	2.8	2.1
<b>7</b>	10	14.0	2.6	72.6	24.9	2.9	4.2
	60	78.3	2.9	72.2	25.0	2.9	3.8
	120	92.9	3.2	72.0	25.0	2.9	
<b>8</b>	10	8.8	2.3	72.1	25.6	2.8	2.6
	60	49.3	2.6	72.0	25.5	2.8	2.5
	120	86.3	2.7	71.7	25.6	2.8	2.1
<b>9</b>	10	16.2	2.8	71.7	25.6	2.8	4.5
	60	80.2	2.7	71.7	25.6	2.8	3.9
	120	94.9	3.3	71.3	25.3	2.8	

Conditions: 20 bar H<sub>2</sub>/CO (1:1), 80°C, toluene, [L] =  $34 \times 10^{-4}$  M, [Rh] =  $1.7 \times 10^{-4}$  M, [oct-1-ene] = 0.84 M;

<sup>a</sup> Percentage of oct-1-ene converted.

<sup>b</sup> Percentage of 2-, 3- and 4-octenes formed.

<sup>c</sup> Turn-over frequency in mole aldehydes formed per mole Rh per hour, averaged over the time given.

in the hydroformylation cycle using triarylphosphine rhodium catalysts this step is rate determining, so that an increase in the TOF is evident. The fact that the n/b ratio for the pyridylphosphines and PPh<sub>3</sub> is the same would imply that in the second reaction step, the alkene migration, the steric environment around the rhodium centre is approximately similar for all these ligands. The higher percentage of isomerised alkene can also be ascribed to the more electrophilic rhodium;

weaker coordination of CO gives more unsaturation and hence more  $\beta$ -elimination.

Apart from 3- and 4-pyridylphosphines we also did some hydroformylation experiments with bis(2-pyridyl)phenylphosphine (**10**). When following the trend this ligand should have a higher rate than ligand **9** due to its two even more electron-withdrawing *ortho*-pyridyl groups. Under standard conditions, however, a very low TOF was found of only  $522 \text{ mol} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$  measured

after 18% conversion, with a n/b ratio of 3.1. To determine which rhodium species was being formed prior to the addition of oct-1-ene, a solution of Rh(acac)(CO)<sub>2</sub> and an excess of **10** in benzene-*d*<sub>6</sub> was stirred under reaction conditions (20 bar syngas, 80°C) after which a sample was taken for <sup>31</sup>P- and <sup>1</sup>H-NMR analysis. When this experiment is performed for PPh<sub>3</sub> the <sup>31</sup>P spectrum shows two hydrides; HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (39.6 ppm, *J*<sub>Rh-P</sub> = 158 Hz) and HRh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (35.6 ppm, *J*<sub>Rh-P</sub> = 146 Hz). In the case of ligand **10** the <sup>31</sup>P spectrum predominantly showed free ligand and no rhodium hydrides. A doublet (22.6 ppm, *J*<sub>Rh-P</sub> = 361 Hz, 2% intensity of the free ligand) along with signals at 147.2 and 146.8 ppm were observed. In the <sup>1</sup>H spectrum two hydride signals can be observed (−9.0 and −10.5 ppm) but these are very low in intensity. So it can be concluded that by using Rh(acac)(CO)<sub>2</sub> as a catalyst precursor hydride formation is not quantitative although reaction of Rh(acac)(CO)<sub>2</sub> and **10** (1:1) quantitatively leads to the formation of Rh(acac)(CO)(**10**) (54.0 ppm, *J*<sub>Rh-P</sub> = 176 Hz). An interesting experiment was to use HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> as a catalyst precursor along with a twenty-fold excess of **10**. Again a slow reaction was observed with a low TOF of only 440 mol · mol<sup>−1</sup> · h<sup>−1</sup> measured after 9% conversion. These results are in contrast with the findings of Wilkinson [12] who performed hydroformylation reactions with tris(2-pyridyl)phosphine and claimed rates similar to that of the PPh<sub>3</sub> system. Our findings show that the *ortho* positioned nitrogen atom is not as inert as the *meta* and *para* nitrogens.

#### 2.4. Catalysis with ligand **2**

As can be seen in Table 1 ligand **2** showed very low catalytic activity under standard hydroformylating conditions in toluene. In 70 min only 1.1% oct-1-ene is converted to aldehydes. This low conversion is most likely due to the low solubility of the active rhodium complex. Addition of the ligand to Rh(acac)(CO)<sub>2</sub> resulted in the formation of a yellow precipitate that proved to

Table 2  
Hydroformylation of oct-1-ene with ligand **2**

Ligand <sup>run</sup>	Time (min)	Conversion (%)	Selectivity (%)			n/b TOF (×10 <sup>−3</sup> )	
			isom	n-ald	b-ald		
<b>2</b> <sup>a</sup>	30	0.5	–	74.3	25.6	2.9	0.05
	70	1.1	–	73.6	26.4	2.8	0.05
<b>2</b> <sup>b</sup>	10	3.0	–	74.1	25.8	2.9	0.90
	60	6.5	2.2	72.5	25.2	2.9	0.32
	120	7.8	2.6	72.4	25.0	2.9	0.19
<b>2</b> <sup>c</sup>	30	9.0	0.9	73.2	26.0	2.8	0.90
	110	40.3	0.9	72.9	26.0	2.8	1.09
	250	87.0	1.1	72.9	25.9	2.8	1.02
<b>2</b> <sup>d</sup>	10	5.1	–	73.9	25.9	2.9	1.5
	65	17.0	0.9	74.0	25.4	2.9	0.80
	230	26.2	0.8	73.7	25.6	2.9	0.34
<b>2</b> <sup>e</sup>	10	5.9	1.1	72.8	26.0	2.8	1.7
	60	32.8	1.0	72.8	26.1	2.8	1.6
	120	64.9	1.3	72.7	26.0	2.8	1.6

<sup>a</sup> Standard conditions (see Table 1).

<sup>b</sup> With Rh<sub>4</sub>(CO)<sub>12</sub> and 34 × 10<sup>−4</sup> M ligand **2**.

<sup>c</sup> With THF as solvent.

<sup>d</sup> With HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> and 34 × 10<sup>−4</sup> M ligand **2**.

<sup>e</sup> With PPh<sub>3</sub> and 34 × 10<sup>−4</sup> M benzoic acid.

be practically insoluble in all common solvents and acidic or basic water. Probably, coordination of the carboxylate group, formed by reaction with the basic acetylacetonate anion in the rhodium precursor, to the rhodium centre results in the formation of polymeric rhodium structures. In a recent publication [21], rhodium carboxylate dimers were reported, in which one carboxylate anion serves as bridging ligand between two rhodium atoms. A complex in which two rhodium nuclei are bridged by two monosulphonated triphenylphosphines, with both the phosphorus and the sulphonate group coordinated to the metal centre, was already reported by Wilkinson [4].

In Table 2 some attempts to optimise the catalytic activity with ligand **2** are listed.

To avoid the presence of the basic acetylacetonate anion, Rh<sub>4</sub>(CO)<sub>12</sub> was used as precursor (*run b*). A relatively high initial TOF was observed but the subsequent TOF's quickly decayed. The reaction mixture in the autoclave was turbid due to the formation of insoluble rhodium structures.

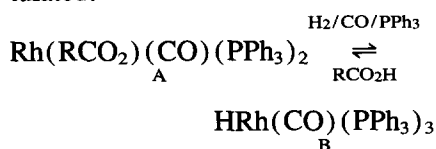
To exclude the possible presence of chloride in the reaction system, triethylamine was added to convert rhodium chloride species. No improvement could be observed.

In order to obtain a homogeneous system the experiment of *run a* has been performed with THF as solvent (*run c*). The hydroformylation reaction proceeded relatively slowly in comparison with triphenylphosphine but complete conversion was obtained. The reaction mixture was homogeneous before and after the reaction. Obviously, THF plays an important role as coordinating solvent in dissolving the active complex(es).

Several attempts have been made to synthesise the catalyst complex  $\text{HRh}(\text{CO})(\mathbf{2})_3$  (**11**) via the route also used for the Wilkinson complex [22]. The yellow complexes thus obtained were insoluble in any common solvent. Formation of the active species by exchange of an excess of ligand **2** with  $\text{PPh}_3$  in Wilkinson's complex  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  has also been attempted. In *run d* a solution of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  and 20 equivalents of ligand **2** in toluene has been prepared and the catalytic activity tested. The initial TOF was the highest yet observed for ligand **2**. The reaction rate nevertheless decreased rapidly and the reaction mixture again showed cloudiness.

It must be concluded that ligand **2** is unsuitable as a ligand in the hydroformylation reaction. Only when THF is used as reaction medium acceptable reaction rates were observed leading to complete conversion. However, THF is a relatively polar solvent which mixes with water and is therefore not suitable for the intended separation system based on aqueous extractions.

Recently, the effect of carboxylic acids on the yield and selectivity of the hydroformylation of hex-1-ene catalysed by rhodium triphenylphosphine complexes has been reported [23]. The authors noticed a significant inhibiting effect of carboxylic acids. The following reaction was postulated:



This reaction was assumed to describe adequately the catalytic system active in the presence of an acid. The shift of equilibrium towards complex A or B depends on the phosphine and acid concentration. The reaction between the carboxylic acid and the hydrido complex B results in a decreased concentration of the active complex B, with concomitant lower catalytic activity.

Reaction between the intramolecular carboxylic group of ligand **2** and the rhodium hydride is likely to lead to the formation of polymeric rhodium structures. The fact that the n/b ratios in *run a–d* are identical to that found with  $\text{PPh}_3$  suggests that the insoluble rhodium complexes are in equilibrium with a dissolved active species, which is very likely to be complex **11**. The low concentration of this active species is then responsible for the observed low reaction rates.

*Run e* clearly demonstrates that the low activity of ligand **2** is caused by its intramolecular carboxylic group. When the hydroformylation was performed with  $\text{PPh}_3$  in the presence of 20 equivalents of benzoic acid, the reaction rates were only somewhat lower and in addition the reaction proceeded to complete conversion.

## 2.5. Two-phase catalysis

Evaluating, it can be concluded that the hydroformylation performance of most of the new ligands is not affected by the additional functional group. In order to investigate the scope of the newly synthesised amphiphilic ligands some preliminary experiments were done involving two-phase catalysis. A two-phase system, prepared by adding water of pH 1.5 to an in situ prepared toluene solution of the rhodium hydride of ligand **4**, showed no catalytic activity upon addition of oct-1-ene. We know [24] that at a pH of 1.5 ligand **4** is quantitatively extracted into the aqueous phase. After the experiment the organic layer was colourless and the aqueous layer had the typical yellow colour of rhodium(I) complexes. This indicates that the ligand, protonated on the nitrogen atom(s), is able to quantitatively transfer the

rhodium into the aqueous phase. This results in a two-phase system in which the rhodium is located in the aqueous phase and the octene in the organic toluene layer. Presumably due to the insolubility of the octene in the aqueous phase no reaction takes place. When the same experiment was performed with water of pH 6 a hydroformylation reaction was observed with a rate comparable with that of the standard homogeneous reaction reported in Table 1. After reaction the aqueous phase was now colourless and the organic phase yellow. Thus, the rhodium is located in the organic phase and the presence of the aqueous phase has no influence.

To improve phase transfer in the experiment which uses the aqueous phase of pH 1.5 lauryl sulphate was added. Although the reaction mixture had the consistency of an emulsion, no reaction was observed. The use of THF as cosolvent had no effect either. To determine the intrinsic catalytic activity of the acidic aqueous layer, hydroformylation of water-soluble alkenes has been attempted. Neither vinyl acetate nor allyl alcohol were converted to the corresponding aldehydes. Since no catalytic activity is observed, it must be concluded that the extracted hydrido-rhodium phosphine complex is not stable in the acidic aqueous phase and decomposes to a cationic rhodium species. This implies that, as we expected, the group of phosphines described in this paper is not suitable for two-phase catalysis, in which the rhodium catalyst is located in an aqueous phase and the substrate in an organic phase. The goal of this work, however, is the use of amphiphilic ligands in a two-step recycling process comprising separation of the products and catalyst via aqueous extraction and redissolving the catalyst in a fresh organic substrate medium. The decomposition of the rhodium hydride in acidic medium described above bears a relation with this two-step recycling process since it shows that the catalyst may not cleanly survive the first step.

The results of the rhodium recovery following the recycling procedure will be described in a subsequent paper.

### 3. Conclusion

The new amphiphilic triphenylphosphine ligands are stable under diverse reaction conditions. In the hydroformylation of oct-1-ene all phosphines act as very suitable ligands. Remarkably, in all cases aldehydes are formed with a *n*/*b* ratio of about 2.8, together with a small percentage of isomerised oct-1-ene. This indicates that the extra functionalities, placed on *meta* or *para* positions, do not have any influence on the selectivity of the hydroformylation reaction. Most ligands show reaction rates comparable with that of PPh<sub>3</sub>. The pyridylphosphines are, however, up to two times faster, which we ascribe to the electron-withdrawing nature of the pyridyl ring.

A plausible explanation for the very low catalytic activity observed for ligand **2**, is that under the reaction conditions polymeric rhodium carboxylate structures are formed. Acceptable rates are observed when the hydroformylation is performed in THF.

Preliminary experiments prove that the group of phosphines described in this paper is not suitable for real two-phase catalysis.

### 4. Experimental

All reactions were carried out in flame-dried glasswork using standard Schlenk techniques under an argon atmosphere. Toluene, THF and diethyl ether were distilled from sodium/benzophenone. All solvents used in the preparation of phosphines were degassed prior to use. Solvents and reagents were distilled prior to use. All chemicals were purchased from Janssen and Aldrich Chemical Co. For column chromatography both Silica gel 60 (Merck) and Aluminium oxide (act. neutral, 50–200 micron, Janssen) were used. The <sup>31</sup>P, <sup>13</sup>C and <sup>1</sup>H NMR spectra were measured on a Bruker AMX 300 spectrometer in CDCl<sub>3</sub> unless otherwise stated. All coupling constants are given in Hz. TMS was used as a standard for <sup>1</sup>H and <sup>13</sup>C NMR and H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR. Mass spectra were measured on a HP 5890/5971 GC–Mass spec-



trometer. Hydroformylation reactions were carried out in a home-made 200 ml stainless steel autoclave. Gas chromatographic analyses were run on a Carlo Erba GC 6000 Vega Series apparatus (split/splitless injector, J and W Scientific, DB1 30 m column, film thickness 3.0  $\mu\text{m}$ , carrier gas: 70 kPa He, FID detector) equipped with a HP 3396 integrator. Syngas 3.0 was purchased from UCAR. The oct-1-ene was freshly distilled from sodium.

#### 4.1. Diphenyl(3-methoxyphenyl)phosphine

A 2.5 M solution of n-butyllithium in hexane (0.020 mol, 8.0 ml) was dissolved in THF (30 ml) at 0°C. The solution was cooled to -78°C and 3-bromoanisole (0.020 mol, 2.56 ml), dissolved in THF (30 ml), was added in 10 min. Stirring of the resulting yellowish suspension was continued for 1 h at -40°C. At -78°C a solution of chlorodiphenylphosphine (0.019 mol, 3.41 ml) in THF (10 ml) was added in 45 min. After stirring overnight at room temperature a saturated aqueous  $\text{NH}_4\text{Cl}$  solution (20 ml) and  $\text{Et}_2\text{O}$  (60 ml) were added. The organic phase was separated and concentrated in vacuum. The remaining oil was dissolved in hot ethanol and cooled to -20°C. The product separated as an oil, which solidified in vacuum. Together with a second crop of crystals the overall yield was 70% (0.013 mol, 3.89 g) of a white solid. The melting point was in accord with the literature value (60–61°C) [12].

$^1\text{H}$  NMR  $\delta$  7.40–7.24 (m, 11H, arom), 6.95–6.85 (m, 3H, arom), 3.74 (s, 3H,  $\text{OCH}_3$ );  $^{31}\text{P}$  NMR  $\delta$  -4.2.

#### 4.2. Diphenyl(3-hydroxyphenyl)phosphine (1)

This compound was prepared according to a modified literature procedure [14]. A mixture of diphenyl(3-methoxyphenyl)phosphine (0.057 mol, 16.6 g), 48% HBr (120 ml), 50%  $\text{H}_3\text{PO}_2$  (9 ml) and a little KI (about 0.1 g) was stirred at 80°C for half an hour and then refluxed for 2 h. On cooling, the HBr adduct of the product separated as an oil which crystallised overnight. The

liquid was removed and the solid was washed with water ( $2 \times 80$  ml). The sticky solid was dissolved in THF (10 ml) and toluene (15 ml) and the solvents were evaporated in order to remove water. After thorough evaporation the crude product was purified by column chromatography (silica gel, 10% MeOH/ $\text{CH}_2\text{Cl}_2$ ) under argon. The product solidified within 2 weeks. Yield 69% (0.039 mol, 10.95 g) of a white solid.

$^1\text{H}$  NMR  $\delta$  7.37–6.71 (m, 14H, arom), 4.9 (br. s, 1H, OH);  $^{31}\text{P}$  NMR  $\delta$  -4.6; m.p. 77–80°C.

#### 4.3. Diphenyl(4-carboxyphenyl)phosphine (2)

A 2 l three-necked, round-bottomed flask was charged with 1 l of anhydrous liquid ammonia. Sodium metal (0.333 mol, 7.67 g) was added in 1 g pieces resulting in a blue-coloured solution. Triphenylphosphine (0.167 mol, 43.7 g) was added in small portions over 40 min. After 2.5 h, the red–orange solution of  $\text{NaPPh}_2$  and  $\text{NaNH}_2$  was treated with 4-chlorobenzoic acid (0.167 mol, 26.1 g) added in 40 min, followed by the addition of THF (500 ml). The reaction mixture was stirred overnight at RT during which the ammonia evaporated, and was then refluxed for 24 h. The THF was evaporated and water (700 ml) was added. The aqueous phase was washed with  $\text{Et}_2\text{O}$  (300 ml), filtered, acidified to pH 2 with conc. HCl, and extracted with  $\text{CH}_2\text{Cl}_2$  (400 ml). The organic phase was evaporated and crystallisation from MeOH/ $\text{H}_2\text{O}$  gave white crystals. Yield 29.5% (0.059 mol, 15.1 g).

$^1\text{H}$  NMR  $\delta$  8.03 (dd, 2H,  $\text{CH}_2\text{COOH}$  arom,  $^3J_{\text{H,H}}=8.1$ ,  $^4J_{\text{P,H}}=0.5$ ), 7.39–7.31 (m, 12H, arom);  $^{31}\text{P}$  NMR  $\delta$  -4.6;  $^{13}\text{C}$  NMR  $\delta$  172.75 (s, COOH), 146.00 (d, CP,  $^1J_{\text{C,P}}=14.3$ ), 136.55 (d, CP,  $^1J_{\text{C,P}}=10.6$ ), 134.60 (d, arom,  $^2J_{\text{C,P}}=20.4$ ), 133.61 (d, arom,  $^2J_{\text{C,P}}=20.4$ ), 130.04 (d, arom,  $^3J_{\text{C,P}}=6.0$ ), 129.82 (s, arom), 129.71 (s,  $\text{C}_\text{COOH}$ ), 129.32 (d, arom,  $^3J_{\text{C,P}}=6.8$ ); m.p. 148–150°C.

#### 4.4. (4-Bromobenzyl)diethylamine

A solution of 4-bromobenzyl bromide (0.16 mol, 40.0 g) in  $\text{Et}_2\text{O}$  (100 ml) was added to an

excess of diethyl amine (1.45 mol, 150 ml) in 1 h. The reaction is slightly exothermic. After stirring for 2 h the precipitate was filtered off and washed with Et<sub>2</sub>O. The filtrate was concentrated and the product was purified by flash column chromatography (silica gel, 40% EtOAc/hexane) giving a yellowish oil. Yield 89% (0.142 mol, 34.24 g).

<sup>1</sup>H NMR δ 7.43 (d, 1H, arom, <sup>3</sup>J=8.22), 7.23 (d, 1H, arom, <sup>3</sup>J=8.21) 3.50 (s, 2H, CH<sub>2</sub>), 2.49 (q, 4H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J=7.10), 1.03 (t, 6H, CH<sub>3</sub>); <sup>13</sup>C NMR δ 139.84 (CCH<sub>2</sub> arom), 131.75 (CH arom), 131.00 (CH arom), 120.91 (CBr arom), 57.54 (CH<sub>2</sub>N), 47.35 (CH<sub>2</sub>CH<sub>3</sub>), 12.42 (CH<sub>3</sub>); mass spectrum *m/e* 241/243 (M<sup>+</sup>), 226/228 (M<sup>+</sup> - CH<sub>3</sub>), 169/171 (M<sup>+</sup> - N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

#### 4.5. [4-(*N,N*-Diethylaminomethyl)phenyl]diphenylphosphine (3)

A 2.5 M solution of *n*-butyllithium in hexane (0.030 mol, 12.0 ml) was dissolved in THF (50 ml) at 0°C. This solution was cooled to -78°C and a solution of (4-bromobenzyl)diethylamine (0.029 mol, 7.12 g) in THF (20 ml) was added in 45 min. Stirring was continued at -30°C for 30 min. At -78°C a solution of chlorodiphenylphosphine (0.028 mol, 5.0 ml) in THF (10 ml) was added in 30 min. The reaction mixture was allowed to warm to room temperature overnight. Water (30 ml) and Et<sub>2</sub>O (20 ml) were added. The organic phase was separated and evaporated. The residue was dissolved in toluene, dried on Na<sub>2</sub>SO<sub>4</sub> and concentrated. After washing two times with a little cold hexane a yellow oil was obtained. Yield 60% (0.017 mol 5.8 g).

<sup>1</sup>H NMR δ 7.36–7.23 (m, 14H, arom), 3.58 (s, 2H, CH<sub>2</sub>), 2.55 (q, 4H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J=7.13), 1.05 (t, 6H, CH<sub>3</sub>); <sup>31</sup>P NMR δ -5.6; <sup>13</sup>C NMR δ 141.54 (s, CCH<sub>2</sub>N arom), 138.07 (d, CP phenyl, <sup>1</sup>J<sub>C,P</sub>=11.3), 135.55 (d, CP phenylCH<sub>2</sub>N, <sup>1</sup>J<sub>C,P</sub>=11.3), 134.40 (s, CH arom), 134.14 (s, CH arom), 129.64 (d, CH arom, <sup>2</sup>J<sub>C,P</sub>=6.0), 129.23 (s, CH arom), 129.02 (d, CH arom, <sup>2</sup>J<sub>C,P</sub>=5.3), 57.82 (s, CH<sub>2</sub>N), 47.38 (s,

CH<sub>2</sub>CH<sub>3</sub>), 12.36 (s, CH<sub>3</sub>); mass spectrum *m/e* 347 (M<sup>+</sup> - 1), 275 (M<sup>+</sup> - 1-N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

#### 4.6. Bis[4-(*N,N*-diethylaminomethyl)phenyl]phenylphosphine (4)

A solution of (4-bromobenzyl)diethylamine (0.075 mol, 18.15 g) in THF (80 ml) was added to magnesium (0.077 mol, 1.86 g), which was activated by 1,2-dibromoethane, in such a rate that the reaction mixture refluxed gently. After the addition the reaction mixture was refluxed for an additional 3 h. At -78°C a solution of dichlorophenylphosphine (0.037 mol, 5.0 ml) in THF (10 ml) was added in 15 min. The reaction mixture was allowed to warm to room temperature overnight and the work-up procedure was used as described for compound 3. No further purification was needed. Yield 64% (0.024 mol, 10.3 g) of a yellow oil.

<sup>1</sup>H NMR δ 7.34–7.23 (m, 13H, arom), 3.61 (s, 4H, CH<sub>2</sub>), 2.54 (q, 8H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>J=7.14), 1.05 (t, 12H, CH<sub>3</sub>); <sup>31</sup>P NMR δ -6.3; <sup>13</sup>C NMR δ 141.40 (s, CCH<sub>2</sub>N arom), 138.00 (d, CP phenyl, <sup>1</sup>J<sub>C,P</sub>=11.3), 135.99 (d, CP phenylCH<sub>2</sub>N, <sup>1</sup>J<sub>C,P</sub>=11.3), 134.33 (s, CH arom), 134.07 (s, CH arom), 129.54 (d, CH arom, <sup>1</sup>J<sub>C,P</sub>=6.8), 129.12 (s, CH arom), 128.92 (d, CH arom, <sup>1</sup>J<sub>C,P</sub>=6.0), 57.85 (s, CH<sub>2</sub>N), 47.36 (s, CH<sub>2</sub>CH<sub>3</sub>), 12.36 (s, CH<sub>3</sub>); mass spectrum *m/e* 432 (M<sup>+</sup> - 1), 360 (M<sup>+</sup> - 1-N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>), 288 (M<sup>+</sup> - 1-2 × N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>).

#### 4.7. (4-Bromobenzyl)diphenylamine

Diphenylamine (0.15 mol, 25.35 g) and KOH (0.6 mol, 33.7 g) were added to a solution of polyethylene glycol methyl ether (mol wt. 350, 0.15 mol, 52.5 g) in toluene (200 ml). Subsequently, 4-bromobenzyl bromide (0.3 mol, 75.0 g) was added and the reaction mixture was refluxed for 72 h. Water (100 ml) and saturated aqueous NH<sub>4</sub>Cl solution (50 ml) were added and the two resulting layers were separated. The organic layer was washed with saturated aqueous NH<sub>4</sub>Cl solution (80 ml), dried on MgSO<sub>4</sub> and

evaporated. Part of the product crystallised and was separated. The remaining oil was purified by flash column chromatography (Basic alumina oxide 58 Å, 50% toluene/hexane). The crystals and the column fractions containing almost pure product were combined and recrystallised from EtOH. Yield 18.6% (0.028 mol, 9.41 g) of white crystals.

$^1\text{H}$  NMR  $\delta$  7.44–6.96 (m, 14 H, arom), 4.95 (s, 2H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR  $\delta$  148.38 (NC arom), 138.84 ( $\text{CCH}_2$  arom), 132.25 (CH arom), 129.94 (CH arom), 128.91 (CH arom), 122.21 (CH arom), 121.24 (CH arom), 121.11 (CBr arom), 56.38 ( $\text{CH}_2$ ); mass spectrum  $m/e$  337/339 ( $\text{M}^+$ ), 169/171 ( $\text{M}^+ - \text{NPh}_2$ ); m.p. 86.5–87.5°C.

#### 4.8. Diphenyl[4-(*N,N*-diphenylaminomethyl)phenyl]phosphine (5)

A 2.5 M solution of *n*-butyllithium in hexane (9.45 mmol, 3.78 ml) was dissolved in THF (20 ml) at 0°C. This solution was cooled to –78°C and (4-bromobenzyl)diphenylamine (9.0 mmol, 3.05 g), dissolved in THF (20 ml), was added in 15 min. Stirring was continued at –40°C for 30 min. At –78°C a solution of chlorodiphenylphosphine (8.82 mmol, 1.57 ml) in THF (10 ml) was added in 30 min. The reaction mixture was allowed to warm to room temperature overnight and the work-up procedure was used as described for compound 3. Crystallisation from hexane/chloroform gave cream-coloured crystals. Yield 62.4% (5.5 mmol, 2.44 g).

$^1\text{H}$  NMR  $\delta$  7.34–7.21 (m, 18H, arom), 7.05 (dist. d, 4H, arom), 6.94 (dist. t, 2H, arom), 5.00 (s, 2H,  $\text{CH}_2$ );  $^{31}\text{P}$  NMR  $\delta$  –4.6;  $^{13}\text{C}$  NMR  $\delta$  148.59 (s, CN arom), 140.74 (s,  $\text{CCH}_2\text{N}$  arom), 137.88 (d, CP phenyl,  $^1J_{\text{C,P}} = 10.6$ ), 136.09 (d,  $\text{CP phenylCH}_2\text{N}$ ,  $^1J_{\text{C,P}} = 10.6$ ), 134.62 (d, CH arom,  $^2J_{\text{C,P}} = 21.9$ ), 134.34 (d, CH arom,  $^2J_{\text{C,P}} = 21.9$ ), 129.91 (s, CH arom), 129.31 (s, CH arom), 129.10 (d, CH arom,  $^3J_{\text{C,P}} = 6.8$ ), 127.34 (d, CH arom,  $^3J_{\text{C,P}} = 6.8$ ), 122.09 (s, Ph–N arom), 121.30 (s, Ph–N arom), 56.77 (s,  $\text{CH}_2$ );

mass spectrum  $m/e$  443 ( $\text{M}^+$ ), 275 ( $\text{M}^+ - \text{NPh}_2$ ); m.p. 115–116°C.

#### 4.9. (4-Bromobenzyl)methylphenylamine

A solution of *N*-methylaniline (0.060 mol, 6.5 ml) in THF (40 ml) was cooled to –65°C. A 2.5 M solution of *n*-butyllithium in hexane (0.063 mol, 25.2 ml) was added in 30 min. The resulting white suspension was warmed to room temperature. In 30 min a solution of 4-bromobenzyl bromide (0.059 mol, 14.85 g) in THF (80 ml) was added. After 3 h of stirring the reaction was completed and water (50 ml) was added. The layers were separated and the organic layer was dried on  $\text{MgSO}_4$  and evaporated. The brown residue was purified by flash column chromatography (silica gel, 40% toluene/hexane) giving a colourless oil. Yield 70% (0.042 mol, 11.6 g).

$^1\text{H}$  NMR  $\delta$  7.46–7.43 and 7.14–7.11 (AB, 4H, arom,  $^3J = 8.3$ ), 7.24 (m, 2H, arom), 6.75 (m, 3H, arom), 4.49 (s, 2H,  $\text{CH}_2$ ), 3.02 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}$  NMR  $\delta$  150.18 (NC arom), 138.80 ( $\text{CCH}_2$  arom), 132.34 (CH arom), 129.95 (CH arom), 129.22 (CH arom), 121.28 (CBr arom), 117.60 (CH arom), 113.18 (CH arom), 56.86 ( $\text{CH}_2$ ), 39.26 ( $\text{CH}_3$ ); mass spectrum  $m/e$  275/277 ( $\text{M}^+$ ), 169/171 ( $\text{M}^+ - \text{N}(\text{CH}_3)\text{Ph}$ ).

#### 4.10. Bis[4-(*N*-methyl-*N*-phenylaminomethyl)phenyl]phenylphosphine (6)

A 2.5 M solution of *n*-butyllithium in hexane (15.0 mmol, 6.0 ml) was dissolved in THF (20 ml) at 0°C. This solution was cooled to –78°C and (4-bromobenzyl)methylphenylamine (15.0 mmol, 4.14 g), dissolved in THF (20 ml), was added in 15 min. Stirring was continued at –50°C for 30 min. At –78°C a solution of dichlorophenylphosphine (7.42 mmol, 1.0 ml) in THF (10 ml) was added in 15 min. The reaction mixture was allowed to warm to room temperature overnight and the work-up procedure was used as described for compound 3. The crude product was purified by column chromatography (silica gel, 20%

Et<sub>2</sub>O/ hexane) under argon. Yield 72% (5.34 mmol, 2.7 g) of a colourless oil.

<sup>1</sup>H NMR δ 7.33–7.18 (m, 17H, arom), 6.72 (m, 6H, arom), 4.53 (s, 4H, CH<sub>2</sub>), 3.02 (s, 6H, CH<sub>3</sub>); <sup>31</sup>P NMR δ –4.6; <sup>13</sup>C NMR δ 150.21 (s, CN arom), 140.52 (s, CCH<sub>2</sub>N arom), 138.06 (d, CP phenyl, <sup>1</sup>J<sub>C,P</sub> = 11.3), 136.23 (d, CP phenylCH<sub>2</sub>N, <sup>1</sup>J<sub>C,P</sub> = 11.3), 134.60 (d, CH arom, <sup>2</sup>J<sub>C,P</sub> = 19.6), 134.29 (d, CH arom, <sup>2</sup>J<sub>C,P</sub> = 19.6), 129.81 (s, CH arom), 129.32 (s, CH arom), 129.12 (d, CH arom, <sup>1</sup>J<sub>C,P</sub> = 6.0), 127.50 (d, CH arom, <sup>1</sup>J<sub>C,P</sub> = 6.8), 117.22 (s, Ph–N arom), 112.92 (s, Ph–N arom), 57.02 (s, CH<sub>2</sub>), 39.30 (s, CH<sub>3</sub>); mass spectrum *m/e* 500 (M<sup>+</sup>), 394 (M<sup>+</sup> – N(CH<sub>3</sub>)Ph).

#### 4.11. Phenylbis(3-pyridyl)phosphine (9)

A 2.5 M solution of *n*-butyllithium in hexane (30 mmol, 12 ml) was cooled to –78°C. A solution of 3-bromopyridine (30 mmol, 2.9 ml) in Et<sub>2</sub>O (50 ml) was added in 1 h. The yellow suspension was stirred for 1 h. At –78°C a solution of dichlorophenylphosphine (11.25 mmol, 1.52 ml) in Et<sub>2</sub>O (15 ml) was added in 30 min. Stirring was continued at –50°C for 30 min. The temperature was allowed to rise to –40°C at which temperature the reaction mixture was quenched with water (ca. 0.5 ml). The temperature was allowed to warm to room temperature overnight. After evaporation the residue was extracted with toluene (2 × 40 ml). The toluene was dried on Na<sub>2</sub>SO<sub>4</sub> and evaporated. The orange oil was purified by column chromatography (silica gel, 5% MeOH/CH<sub>2</sub>Cl<sub>2</sub>) under argon. Yield 53% (6.0 mmol, 1.57 g) of a yellowish oil.

<sup>1</sup>H NMR δ 8.60–8.53 (m, 4H, H<sub>2+6</sub>), 7.60–7.55 (m, 2H, H<sub>4</sub>), 7.40–7.26 (m, 7H, Ph + H<sub>5</sub>); <sup>31</sup>P NMR δ –17.7; <sup>13</sup>C NMR δ 154.61 (d, C<sub>2</sub>, <sup>2</sup>J<sub>C,P</sub> = 24.16), 150.62 (s, C<sub>6</sub>), 141.47 (d, C<sub>4</sub>, <sup>2</sup>J<sub>C,P</sub> = 16.61), 134.80 (d, C<sub>i</sub>, <sup>1</sup>J<sub>C,P</sub> = 9.80), 134.22 (d, C<sub>o</sub>, <sup>2</sup>J<sub>C,P</sub> = 20.38), 132.87 (d, C<sub>3</sub>, <sup>1</sup>J<sub>C,P</sub> = 15.86), 130.18 (s, C<sub>p</sub>), 129.55 (d, C<sub>m</sub>, <sup>3</sup>J<sub>C,P</sub> = 6.82), 124.23 (broad s, C<sub>5</sub>); mass spectrum *m/e* 264 (M<sup>+</sup>).

#### 4.12. The hydroformylation experiments

In a typical experiment the autoclave was filled with a mixture of a 4 mM solution of Rh(acac)(CO)<sub>2</sub> in toluene (0.004 mmol, 1 ml), the ligand (0.08 mmol) and 19 ml toluene, under an atmosphere of argon. The autoclave was pressurised with syngas (CO:H<sub>2</sub> = 1:1) to 20 bar and the temperature was raised to 80°C in approximately 40 min. Subsequently, oct-1-ene (20 mmol, 3.14 ml) and decane (3 mmol, 0.6 ml) as internal standard was added under pressure. The samples were analysed by Gas Chromatography. The conversion, isomerisation and *n/b* ratios were determined by the integrated areas which were corrected for the RMR values of the octenes (778) and C<sub>9</sub>-aldehydes (800).

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