Rhodium catalysed hydroformylation of higher alkenes using amphiphilic ligands: part 2

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Abstract

The performance of a new rhodium recycling system is described using a series of amphiphilic ligands: Ph_2ArP (Ar = 3-hydroxyphenyl, 4-carboxyphenyl), $Ph_nAr_{3-n}P$ (Ar = $4-PhCH_2X$, X = NEt_2, NMePh, NPh_2; n = 1-2) and $Ph_nAr_{3-n}P$ (Ar = 3-pyridyl, 4-pyridyl; n = 1-2). The corresponding rhodium complexes are active in the hydroformylation of oct-1-ene and can be separated from the product aldehydes by acidic or basic extraction into water. After neutralisation of the aqueous phase the rhodium phosphine species can be extracted into a new batch of oct-1-ene, with toluene as organic solvent. The pH-depending distribution characteristics of the free ligands have been determined. $PhAr_2P$ with Ar = $4-PhCH_2NEt_2$ and Ar = 3-pyridyl were completely extracted from a solution in Et_2O or toluene into a H_2SO_4-solution of pH 3 and 2, respectively. Recycling experiments with the former ligand demonstrated that the catalytically active rhodium hydrides decompose during the acidic extraction step. The structure of the recovered rhodium complexes could not be elucidated by NMR- and IR-analysis. Rhodium measurements by ICP-AES established that rhodium was quantitatively recycled. Pressurising the recovered rhodium and excess ligand to 20 bar syngas at 80°C resulted in regeneration of the original, catalytically active species. A retention of catalytic activity up to 87% was achieved.

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

1. Introduction

The industrial hydroformylation of higher alkenes is still performed with cobalt based catalysts in spite of the enormous progress that has been made in the application of rhodium catalysts in the last decades [1–6]. Cobalt based catalytic systems use the cheaper internal alkenes as substrates, but even if terminal alkenes would be used, there is as yet no economic rhodium based system available for the production of higher oxygenates via hydroformylation. Separation of the expensive rhodium and the high-boiling aldehydes is still the main obstacle for commercial application of the more active and selective rhodium catalysts.

The use of water-soluble catalysts in a biphasic system has received much attention [1,7–20].

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The application of this system, however, is limited by the solubility of the substrates in water. While propene can be successfully hydroformylated in a two-phase system [21], the activity of this catalyst system for higher alkene homologues is at least an order of magnitude lower, due to their low solubility in water. The use of surface-active agents [22,23], or ligands which have surface active properties themselves [24,25], may enhance solubility but will inevitably have a negative influence on the ease of separation which can result in rhodium loss. In some cases, water can also interfere with catalysis and can strongly influence the result [26–29].

We already reported on the development of a separation approach which differs from two-phase catalysis [30,31]. This recycling system is based on the use of an amphiphilic rhodium catalyst which is not solely restricted to water, but can switch between an organic and an aqueous phase by varying the pH of the system. The major benefit of our system is that the catalysis takes place in a homogeneous, organic phase with a concomitantly high reaction rate. In Fig. 1, the principle of this recycling system is pictured.

The neutral amphiphilic catalyst is located in an organic medium, which may be the pure substrate. After the hydroformylation reaction the organic phase is washed with water of the appropriate pH. At this pH the catalyst and excess ligand become water-soluble, either by protonation or deprotonation, and they are extracted in the aqueous phase at which point the organic products can be separated from the catalyst. The cycle can be completed by neutralisation of the aqueous phase and extracting the catalyst and excess ligand into a new batch of substrate. A disadvantage of this system is that it also produces salts, albeit in catalytic quantities only.

For cobalt, this method has long been industrially applied in the Kuhlmann hydroformylation process [32]. The acidic complex $HCo(CO)_4$ in this process is deprotonated and extracted
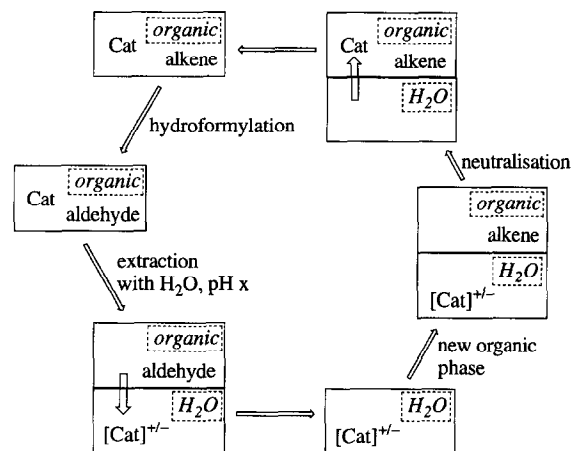

Fig. 1. Schematic representation of the recycling system.

into water. An early report [33] described a cobalt carbonyl complex containing the amino-functionalised phosphine $P(CH_2CH_2NEt_2)_3$. This complex was said to be extractable into dilute carbonic acid and could be re-extracted into an organic phase by simply reducing the CO_2 pressure.

For rhodium, this recycling approach has received little attention so far [34–37]. Wilkinson's attempts to extract the rhodium complex of tris(2-pyridyl)-phosphine were unsuccessful [34]. Bayon et al., however, could precipitate dinuclear rhodium thiolates, which were functionalised with amino groups, as the ammonium sulphate salt by adding sulphuric acid [35]. This solid could be reused after neutralisation without loss of activity. Tóth et al. [36] showed that the rhodium complex of amino-functionalised skewphos could be recycled after hydrogenation by acidic extraction in dilute HBF_4 and subsequent neutralisation by NEt_3.

In a previous report [30], we described the synthesis of a series of amphiphilic triphenylphosphine ligands (see Fig. 2). In the present work the pH-depending distribution characteristics of the free ligands are determined. The efficiency of the rhodium recycling system using the series of modified phosphines is established in terms of retention of catalytic activity

3 n=2, X=NEt₂
4 n=1, X=NEt₂
5 n=2, X=NPh₂
6 n=1, X=NMePh

7 n=2, 4-pyridyl
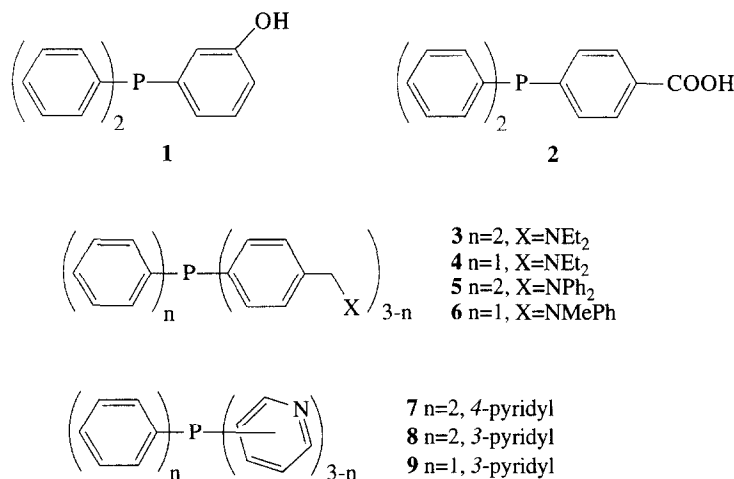8 n=2, 3-pyridyl
9 n=1, 3-pyridyl

Fig. 2. The amphiphilic ligands.

and rhodium recovery, as measured by inductive coupled plasma atomic emission spectrometry measurements (ICP–AES).

2. Results and discussion

2.1. Distribution characteristics of the free ligands

The pH-depending distribution characteristics were determined by adding water of several pH-values (H_2SO_4- or KOH-solutions) to a solution of the ligand in Et_2O and measuring the UV-adsorption spectra of both layers [31]. Prior, the extinction coefficient of the ligand in both

Et_2O and water was determined at selected wavelengths (Table 1). The concentrations of the ligand in both layers could then be expressed, at each specific final pH-value, in the distribution coefficient D.

$$D = \frac{C(H_2O)}{C(H_2O) + C(org)} \times 100\%$$

2.1.1. Ligands 1–2

From Fig. 3, it can be concluded that the more acidic ligand 2 is extracted into the aqueous phase at a lower pH than ligand 1. The phenol group in ligand 1 is too weakly acidic and at pH 14 only 22% of the ligand was

Table 1
The selected wavelengths and corresponding extinction coefficients

Ligand	Organic solution		Aqueous solution	
	λ (nm)	$\epsilon(\lambda) \times 10^{-4}$	λ (nm)	$\epsilon(\lambda) \times 10^{-4}$
1	280	0.94	306	0.50
2	285	1.06	280	1.05
3	266	1.14	268	0.41
4	266	1.39	270	0.74
6	280	2.01	270	0.83
7	266	1.17	320	0.70
8	260	0.88	252	1.31
9	259	1.16	245	1.66
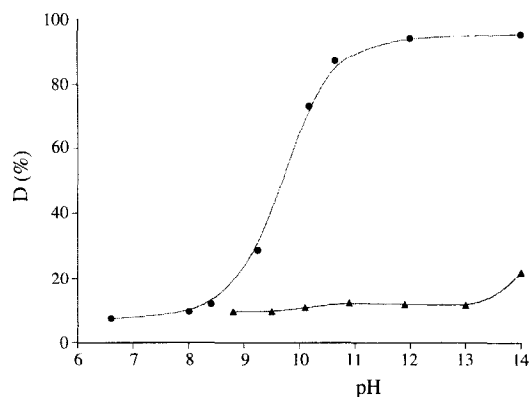
Fig. 3. Extraction curves of ligand 1 (▲) and 2 (●).

extracted. Ligand **2**, however, was quantitatively extracted at the relatively mild pH 12.

At pH 6.6 still 8% of the ligand is located in the aqueous phase. The solubility of the ligand in its neutral state in water was tested and proved negligible. The formation of persistent micro emulsions and/or micelles is hold responsible for transferring a small amount of ligand into the aqueous layer. This is a result of the surface active properties of the ligands [24,25].

2.1.2. Ligands 3–6

In Fig. 4 the D–pH plots are depicted for the phosphines functionalised with the benzylic amines. A clear correlation between the ease of extraction and the basicity of the amino group was observed. Ligand **5**, containing the weakly basic diphenylamino group, was not even soluble in a hot aqueous 1 M H_2SO_4-solution. When the molarity of the H_2SO_4-solution was increased to 3 M the ligand slowly dissolved which was most likely due to protonation of both nitrogen and phosphorous atoms. Evidently, the basicity of the two somewhat more basic amino groups in ligand **6** is still too low to render the hydrophobic ligand containing five phenyl rings soluble in water. At pH 0 still less than 50% of the ligand was present in the aqueous phase.

From Fig. 4 it can be seen that phosphines **3** and **4** with the strongly basic benzylic dieth-
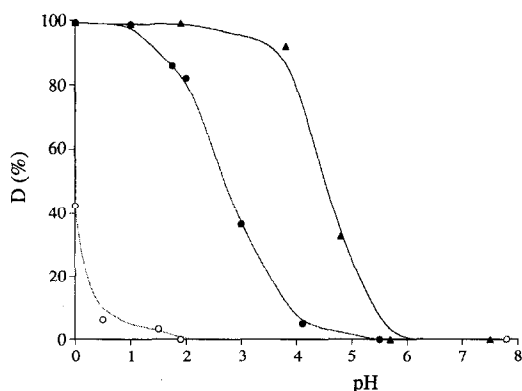
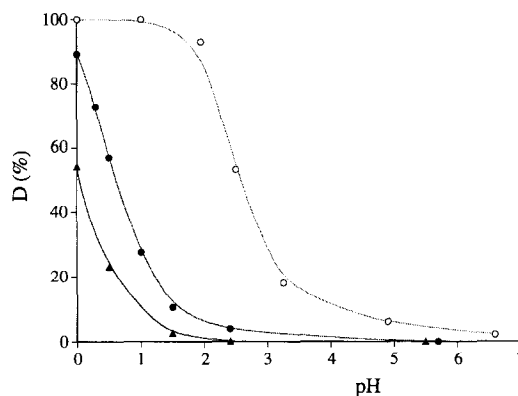Fig. 4. Extraction curves of ligand **3** (●), **4** (▲) and **6** (○).

Fig. 5. Extraction curves of ligand **7** (●), **8** (▲) and **9** (○).

ylamino group were extracted at higher pH-values. These curves show that by variation of the number of functional groups, the extraction point can be adjusted. Just as important is the fact that both ligands were located completely in the organic phase at neutral pH-values (> 5.5).

2.1.3. Ligands 7–9

The extraction curves of the pyridyl–phosphines are pictured in Fig. 5. Also here the trend of increasing ease of extraction with increasing basicity was obvious. Ligand **7**, with its *para*-pyridyl ring, was more readily extracted than ligand **8**, with its less basic *meta*-pyridyl ring, but extraction was still incomplete at pH 0.

The effect of the two *meta*-pyridyl rings in ligand **9** is dramatic, and complete extraction was observed at pH 2.

Summarising, from the extraction data it was concluded that ligands **1**, **5** and **6** cannot be quantitatively extracted while ligand **2**, in spite of its promising extraction behaviour, is unsuitable due to its low catalytic activity [30]. Ligands **4** and **9** were selected for further studies because they can be transferred between the aqueous and organic phase within a narrow and relatively mild pH-range.

2.2. Rhodium recycling experiments

The efficiency of the rhodium recycling system using the new amphiphilic ligands was

determined in two ways. The first method involves subjection of the recovered rhodium to a second hydroformylation run and comparison of the observed catalytic activity with that of the original activity in the first run. Obviously, this retention of activity is just an indication of the minimal amount of rhodium recovered, as not all recovered rhodium may be catalytically active. Second, determination of the absolute amount of rhodium (metal) recovered was done by ICP–AES.

Optimisation of the recycling procedure was done for ligand **4**. In Table 2 the results of the most important recycling experiments are summarised. The procedure for a standard experiment (entry 1, Table 2) is described in the Experimental section. For each experiment the crucial variations in experimental conditions are

given. The hydroformylation reaction is first order in oct-1-ene concentration and so is the turn-over-frequency (TOF). The TOF of the first run (TOF1) is taken as mol of aldehyde formed per mol of rhodium averaged over the first 30 min. Since the turn-over frequency of the second run (TOF2) was determined after a similar conversion of oct-1-ene, the quotient of both turn-over-frequencies is a measure for the recovery of catalytically active rhodium and is referred to as the retention of activity (RA).

From Table 2, it can be seen that rhodium and excess ligand can be recycled and oct-1-ene can indeed be hydroformylated in a second run. The selectivity (n/i-ratio of 2.8) was exactly the same as in the first run. However, the recovery of catalytic activity was low. Catalytic activity due to adsorbed rhodium on the wall of

Table 2
Summarised results of the recycling experiments

Entry	Conditions [a]	TOF1 [b]	TOF2 [b]	RA (%) [c]
Ligand 4				
1	Extraction with H_2SO_4 (pH 1.8), neutr. with $NaHCO_3$ (pH 7).	1621	342	21
2	Recycling done under 1 bar syngas (as 1).	1630	526	32
3	Autoclave content was cooled prior to extraction (as 1).	1619	998	62
4	Extraction with HBF_4 (pH 1.8) (as 3).	1522	643	43
5	Extraction with p-TSA (pH 1.8) (as 3).	1513	879	58
6	Extraction with pH 1.5 (H_2SO_4) (as 3).	1568	964	61
7	Extraction; $6 \times$ pH 2.2 (H_2SO_4) [e]	1523	1266	83
8	Extraction; $8 \times$ pH 2.3 (H_2SO_4) [e]	1530	992	65
9	Regeneration time prior to second run was 3 h (as 3).	1625	1026	63
10	Regeneration time of 19 h (as 9).	1595	815	51
11	Regeneration time of 40 h (as 9).	1631	732	45
12	Second run with a 50-fold excess (over Rh) of NEt_3 (as 3).	1568	944	60
13	Regeneration time of 20 h at 100°C/100 bar syngas (as 3).	1565	125	8
14	Neutralisation by NaOH instead of $NaHCO_3$ (as 3).	1582	823	52
15	Neutralisation to pH 6.5–7 (as 7).	1527	1331	87
16	Test reaction [d].	1548	1336	86
Ligand 9				
17	Extraction with H_2SO_4 (pH 1), neutr. with $NaHCO_3$ (pH 6.5).	3439	1936	56
18	Extr.; $5 \times$ pH 1.8 (H_2SO_4), neutr. with $NaHCO_3$ (pH 6–6.5).	3650	2187	60

[a] Given here are the variations on the standard experiment given in brackets.
[b] Turn-over frequency in mol aldehydes formed per mol Rh per h. TOF1 and TOF2 are the values for the first and the second run. See text for a further definition.
[c] Retention of activity, defined as (TOF2/TOF1) × 100%.
[d] Reaction in which the precise recycling procedure was followed, but without the acidic extraction and concomitant neutralisation.
[e] See text for further details.

the autoclave was routinely measured by performing a hydroformylation experiment in the absence of $Rh(acac)(CO)_2$. No activity was observed under these conditions. A simple experiment was done to exclude the possibility of an inhibitory effect of Na_2SO_4. When the catalyst precursor solution was washed with an aqueous Na_2SO_4-solution prior to catalysis a hydroformylation reaction with normal rates was observed.

In Table 3, the results of the rhodium analyses by ICP–AES are summarised. The recovery of rhodium, using ligand **4** under the conditions as described above, is nearly complete (95.7%, entry 1). Apparently, the rhodium and excess ligand are largely recycled, but the rhodium in the eventual toluene phase is only partly catalytically active due to irreversible catalyst decomposition.

2.2.1. NMR-study

To establish in which form the rhodium and excess ligand are present throughout the recycling procedure, NMR-analyses were done. In one experiment, on a small and concentrated scale, oct-1-ene was hydroformylated after which the brownish reaction mixture was sub-
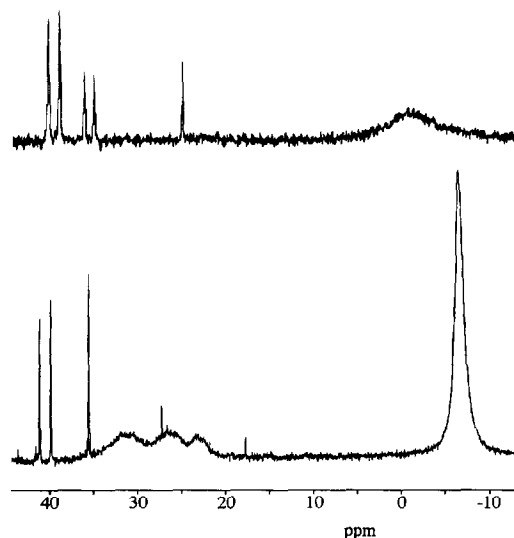

Fig. 6. ^{31}P-NMR spectra of the organic phase prior to acidic extraction (top) and the acidic aqueous phase (bottom).

jected to NMR-analysis prior to acidic extraction. As expected [30], in the ^{31}P-spectrum two hydrides were present (see Fig. 6): $HRh(CO)_2(\mathbf{4})_2$ (35.9 ppm, $J_{Rh-P} = 145$ Hz) and $HRh(CO)(\mathbf{4})_3$ (40.0 ppm, $J_{Rh-P} = 158$ Hz). The resonance at 25 ppm does not originate from phosphine oxide. The ^{1}H-spectrum revealed the broad signals of the two hydrides at -8.9 and -9.2 ppm, respectively. In the case of PPh_3 the

Table 3
Results of rhodium measurements by ICP–AES

Entry	Ligand	Rhodium content (μg)			Rh recovery [f] (%)	Rh balance [g] (%)
		First organic layer	Aqueous layer	New organic layer		
1 [a]	4	45 [h]	33	2239	95.7	96.9
2 [b]	4	71	52	2320	95.0	101.2
3 [c]	4	46	17	2258	97.2	96.0
4 [d]	9	1132	26 [i]	1116	46.0	100.7
5 [e]	9	862	18 [j]	1356	57.0	97.9

The 95%-confidence interval of the mean measured values is $\pm 4.5\%$ for contents > 10 μg, otherwise $\pm 10\%$.
[a] Single extraction with H_2SO_4 (pH 1.5).
[b] Two extractions with H_2SO_4 (pH 1.8).
[c] Seven extractions with H_2SO_4 (pH 2.2) and mild neutralisation to pH 6.5–7.
[d] Single extraction with H_2SO_4 (pH 1).
[e] Six extractions with H_2SO_4 (pH 1.8) and mild neutralisation to pH 6–6.5.
[f] Rhodium recovered in the new organic layer as percentage of the total amount measured.
[g] Rhodium mass balance defined as the total amount of rhodium measured as percentage of the starting amount ($= 2414$ μg).
[h] Persistent emulsion contained 21 μg Rh.
[i] Brown precipitate contained 144 μg Rh.
[j] Brown precipitate contained 127 μg Rh.

former complex is the catalytically active species and the solely detectable species under syngas pressure [38,39]. When the CO atmosphere is replaced by argon in the presence of excess ligand this complex is partly transformed into the latter complex.

Next, the toluene layer was extracted with a H_2SO_4-solution in D_2O. NMR-analysis of the resulting brown aqueous layer did not reveal the presence of an unambiguous rhodium species, as can be seen on Fig. 6.

Remarkably, only a very small fraction of $HRh(CO)(4)_3$ (40.6 ppm, $J_{Rh-P} = 154$ Hz) survived in this acidic environment. The most striking features of this spectrum are the very broad signals between 20–35 ppm. These signals are tentatively ascribed to the presence of polynuclear rhodium phosphine species. The free ligand dominates the spectrum and has a broad signal indicating chemical exchange with complexed ligand. Protonation of the ligand on the phosphorous atom, which is a possible side reaction, was not found to be significant at the applied pH. The resonance at 35 ppm is assigned to phosphine oxide. The ^1H-NMR spectrum of the aqueous layer is not very informative. It predominantly shows the signals of the ligand since no hydride signals could be observed under the acidic conditions due to exchange of the Rh–H bond with D_2O to Rh–D.

Subsequently, the acidic aqueous phase was neutralised and extracted twice with d_8-toluene. The ^{31}P-spectrum of both brown toluene layers exclusively revealed the signal of the free ligand. Both AES measurements and colour indicated that the toluene phase contained rhodium. The absence of signals originating from rhodium phosphine species suggests the formation of rhodium carbonyl complexes without phosphine. Also, the formation of rhodium sulphate or carboxylate complexes cannot be excluded.

The extraction experiment conclusively showed that the catalytically active rhodium hydrides largely decompose already during the first acidic extraction step. The retention of activity obtained sofar, however, implies that

the hydrides can be partly regenerated. An obvious cause of decomposition is the absence of syngas during the recycling procedure. Therefore, the recycling was repeated under 1 bar of syngas, but this had no noticeable influence on the decomposition of the rhodium hydrides (Table 2, entry 2).

NMR analysis also established that the ligand itself survives the recycling procedure, since no significant ^{31}P-signal was measured in the remaining aqueous layer after neutralisation. The use of PPh_3 as internal standard revealed a 90–100% recovery of ligand in the eventual toluene layer.

2.2.2. IR-study

IR-spectroscopy was also used in an attempt to elucidate the structure of the recycled rhodium species. A concentrated solution of $Rh(acac)(CO)_2$ and excess ligand was prepared. Displacement of CO immediately resulted in the formation of $Rh(acac)(CO)(4)$ giving a ν_{CO} band at 1976 cm^{-1}, which is consistent with the value found for the corresponding PPh_3-complex [40]. After being pressurised to 20 bar syngas at 80°C, the catalytic mixture was subjected to IR-analysis prior to the recycling procedure. As expected, a group of ν_{CO} and ν_{Rh-H} bands appeared (1920, 1969, 1991, 2010 and 2037 cm^{-1}) originating from the two hydrides mentioned earlier. In the IR-spectrum of the dark brown toluene layer, obtained after the recycling procedure, these bands were replaced by two somewhat broad ν_{CO} bands at 1975 and 1953 cm^{-1}. So, this experiment shows the presence of a CO-containing species in the recycled toluene phase. The suspected formation of rhodium phosphine carbonyl clusters is unlikely since a bridging CO absorbs at about 1850 cm^{-1} [41].

2.2.3. Acidic extraction

To improve the retention of activity, the first step in the recycling procedure was done under milder conditions. Cooling the reaction mixture in the autoclave to below 10°C prior to acidic

extraction gave a high activity of 62% (Table 2, entry 3).

The role of the applied acid was also examined. HCl was not used since oxidative addition is known to lead to irreversible formation of octahedral Rh(III)-complexes [36,42,43]. H_2SO_4 was used because of its non-coordinating properties though the formation of rhodium sulphate complexes cannot be excluded; a recent report showed the formation of a dimeric rhodium phosphine carbonyl complex bridged by a triflate [41]. When we used HBF_4, instead of H_2SO_4, a brown precipitate was formed at the interphase of the yellowish toluene layer and bright yellow aqueous layer. The activity found (Table 2, entry 4) had significantly decreased. It appeared that the partial formation of insoluble BF_4-complexes resulted in a low rhodium recovery. This was confirmed by an NMR experiment at higher concentrations where the decomposition was complete; a dark brown solid was formed while the aqueous layer remained colourless. The solid was insoluble in any common solvent and could, therefore, not be characterised.

An experiment in which p-toluenesulfonic acid was used resembled the experiment with sulphuric acid, both in behaviour and activity found (Table 2, entry 5).

An important parameter in the acidic extraction step is the concentration of the sulphuric acid in the applied acidic aqueous layer. Increasing the concentration of acid by a factor of two (Table 2, entry 6) going from pH 1.8 to 1.5 made no difference. In another experiment the autoclave content was siphoned into demineralised water (of about pH 5.5). Subsequently, the reaction mixture was titrated with an aqueous H_2SO_4-solution of pH 1.5. When the aqueous layer had a pH-value of 2.2 (calculated from the amount of water and acid), the yellow colour was partly transferred to the aqueous layer indicating that the amino functions were protonated. At this point only part of the amino groups is protonated resulting in partial extraction. Five successive extractions, using water of

pH 2.2, resulted in the quantitative extraction of rhodium into the aqueous phase. A colourless toluene layer remained. The effective pH of the combined aqueous layers was about 5, which is in agreement with the extraction results pictured in Fig. 5. Subsequently, the standard recycling procedure was continued. In this way, 83% activity was found (Table 2, entry 7). The acidic extraction at pH 5, and re-extraction at pH 7, implies that the amount of salt waste is minimal which is important from an industrial point of view.

When the experiment in entry 7 (Table 2) was repeated, with 8 extractions of a H_2SO_4-solution of pH 2.3, only a moderate activity was found. This strongly suggested that a mild acidic extraction is just one of the requisites for a high RA and that the neutralisation step also plays a crucial role.

For obtaining a high RA, mild acidic extraction seems pivotal. The AES measurements (Table 3, entries 1–3) demonstrate that the differences in rhodium losses in the first organic layer are rather small when the extraction acidity is varied. Single extraction with a H_2SO_4-solution of pH 1.5 or two extractions with a H_2SO_4-solution of pH 1.8 both result in a rhodium loss of about 70 μg, compared to the 46 μg rhodium loss under mild conditions.

2.2.4. Neutralisation

During the neutralisation with saturated aqueous $NaHCO_3$-solution, the aqueous phase consistently became turbid which probably is a result of the surface active properties of the ligand. In order to break down the persisting emulsion, several agents were added which are known to improve phase separation, such as tert.-butanol, pentane or a saturated aqueous Na_2SO_4-solution. No improvement was observed. Leaving the reaction mixture for more than 1 h without stirring, eventually resulted in a clear and almost colourless aqueous phase.

Since the structure of the recycled rhodium complexes has not been elucidated, the time needed for the regeneration of the catalytically

active rhodium hydrides is unknown. Therefore, the regeneration time, in which the recovered toluene phase is put under pressure at 80°C prior to addition of the second batch of oct-1-ene, was varied. At least 1 h was needed, which is only somewhat longer than the period needed when Rh(acac)(CO)$_2$ is used as precursor. From entries 9–11 in Table 2, it can be seen that longer periods gave no improvement, and that extensive prolongation of this period presumably leads to thermal decomposition of the catalyst.

Possibly formed rhodium phosphine sulphate complexes can have the same low hydroformylation activity as is known for rhodium chlorides. It has been reported [44] that addition of bases such as amines has a strong promoting effect on such rhodium chloride systems. The reactivating effect of NEt$_3$ in case of sulphates was not observed (Table 2, entry 12). Regeneration under more harsh conditions by pressurising the recovered rhodium to 100 bar syngas at 100°C overnight before performing the second run, was not successful either (Table 2, entry 13).

The formation of rhodium carboxylate complexes has been reported to have a damaging effect on catalytic activity [30,45,46]. The use of carbonic acid can result in similar complexes. When NaOH was used as neutralising base a more persistent emulsion was formed, and the observed activity was even somewhat lower compared to that of the experiment in which NaHCO$_3$ was used.

The experiment with the highest obtained RA yet (Table 2, entry 7) could not be repeated. The subtle acidic extraction was now combined with a more subtle neutralisation procedure. Only small amounts of NaHCO$_3$ were added resulting in a pH between 6.5 and 7. Furthermore, prolonged waiting periods and extraction with 7 portions of toluene were applied (Table 2, entry 15). The observed 87% is the highest observed activity so far. Subsequent experiments irrefutably proved that in order to obtain a high RA, both extraction steps have to be carried out

under very mild conditions, i.e., near neutral pH-values.

The rhodium measurements in Table 3 (ligand 4, entries 1–3) show that the rhodium was largely recovered. Clearly, the use of mild extraction conditions merely diminish the extent of irreversible catalyst decomposition. The rhodium losses in both the toluene and aqueous layer were in the order of 1–3% and probably due to incomplete phase separation (emulsions/micelles). The procedure, comprising both subtle acidic extraction and neutralisation (Table 3, entry 3), suffered somewhat less from rhodium losses in the first and in the second extraction step. This is most likely due to the greater number of extractions. Importantly, in all cases rhodium mass balances were found between 96 and 101%, which implies that there are no significant rhodium losses, other than in the successive layers.

Although the AES data clearly indicate that the rhodium recovery is almost quantitative the highest yet obtained RA did not exceed 87%. Therefore, an experiment was done in which the reaction mixture was removed from the autoclave. The autoclave was washed with toluene and the combined organic phases were concentrated to the original volume. Other experiments already showed that evaporation of the catalytic mixture had no influence on the RA. The so-treated mixture showed a 14% loss of catalytic activity when compared with that of a non-treated mixture (Table 2, entry 16). It had to be concluded that upon releasing the syngas pressure, irreversible decomposition takes place to the extent of 10–15%. It would be very interesting to be able to perform the entire recycling procedure in a closed pressurised system. This clearly is one of the top priorities for further research.

2.2.5. Ligand 9

The most important recycling experiments using ligand 9 are listed in Table 2. This ligand proved to be less successful than ligand 4. As expected, an aqueous H$_2$SO$_4$-solution with a

lower pH was required to extract rhodium and excess ligand into the aqueous layer. Regardless of the pH applied, the toluene layer persistently remained yellow which is indicative of rhodium remaining in the organic phase. Neutralisation of the aqueous phase to pH 6–6.5 in the presence of fresh toluene instantly resulted in a clear colourless aqueous layer and a clear yellow organic layer. A small but significant amount of a green–yellow precipitate was also formed. Single extraction with a H_2SO_4-solution of pH 1 resulted in a retention of activity up to 56% (Table 2, entry 17).

The RA could not be improved by applying multiple acidic extractions with a H_2SO_4-solution of pH 1.8 (Table 2, entry 18). Again, the final organic layer remained yellow. The resulting pH of the aqueous layer after each extraction was 2.5–3. In this pH range, ligand 9 is partly extracted (see Fig. 6). Subsequent neutralisation under mild conditions could not avoid the formation of the precipitate.

In Wilkinson's attempts to recover the rhodium tris(2-pyridyl)phosphine complex with dilute aqueous solutions of HCl or HBF_4, similar observations were made [34]. A significant amount of rhodium remained in the orange organic phase and could not be extracted. Addition of petroleum ether to the reaction mixture did precipitate most of the rhodium complex (ca. 95%) which could be reused.

Rhodium AES analytical data were consistent with the observations made in the recycling experiments. Both the recycling experiments done under normal (Table 3, entry 4) and mildly acidic (Table 3, entry 5) conditions suffered from extensive rhodium losses in the original organic phase. The fraction of the rhodium that was extracted could be largely transferred to the new organic phase. The rhodium content of the aqueous phase is minimal, but the mentioned green–yellow precipitate contained 5–6% rhodium. The procedure, comprising both subtle acidic extraction and neutralisation ensured a slightly better rhodium recovery.

Probably, the active rhodium hydrides of lig-

and 9 also decompose during the acidic extraction step. In contrast with ligand 4, a large fraction of the rhodium species is not extracted in water. While the ligand itself is stable in an acidic environment, the corresponding rhodium complex is not. This can be ascribed to irreversible decomposition at the rhodium centre, due to the presence of the protonated 3-pyridyl ring. However, the water-soluble part could be neutralised and was efficiently extracted into a new organic phase. The RA values in Table 2 are identical with the rhodium recovery percentages, thus all recovered rhodium must be catalytically active.

3. Conclusion

The series of amphiphilic ligands comprises ligands with a variety of different distribution characteristics. The ligand functionalised with the diethylamino groups (4) gave the best results in rhodium recovery experiments. The rhodium recovery of 97% is promising when the simple experimental set-up is taken into consideration. Generally, a commercial rhodium-based process for bulk oxygenates cannot tolerate a rhodium loss higher than 0.1 ppm in the reaction products, which corresponds to a rhodium recovery of 99.98%. The retention of activity of 86% is high, though not satisfactory from an industrial point of view. Future research should clearly focus on minimising the amount of rhodium catalyst that is catalytically inactive after recycling.

4. Experimental

4.1. General

All reactions were carried out in flame dried glasswork using standard Schlenk techniques under an argon atmosphere. Toluene was distilled from sodium/benzophenone. All solvents used were degassed prior to use. All chemicals

were purchased from Janssen and Aldrich Chemical. NMR spectra were measured on a Bruker AMX 300 spectrometer. TMS was used as a standard for ^{1}H- and ^{13}C-NMR and H_3PO_4 for ^{31}P-NMR. Infrared spectra were recorded on a Nicolet 510 FT–IR spectrophotometer. 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 μm, 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 filtered over a short column of aluminum oxide (act. neutral, 50–200 μm, Janssen). UV-spectra were measured on a Varian Cary 4 single beam apparatus. The pH-values were measured on a Corning 240 pH-meter. ICP–AES was measured on a sequential Jarrell Ash upgraded Atomscan Model 2400 ICP scanning monochromator. Further specification of the spectrometer is given elsewhere [47]. The upgrading consists of processor- and software replacements by the Thermo Jarrell Ash Atomscan Model 2.5. Sulphuric acid calibration solutions of rhodium were prepared from a rhodium standard ($RhCl_3$ in 20% HCl) from Johnson Matthey.

The method for measuring the distribution characteristics of the free ligands have been described in a previous paper [31].

4.2. Rhodium recycling experiments

In the experiment of entry 1 (Table 2) the autoclave was filled with a mixture of a 4 mM solution of $Rh(acac)(CO)_2$ in toluene (0.008 mmol, 2 ml), ligand (0.16 mmol) and toluene (14 ml). The autoclave was pressurised with syngas ($CO/H_2 = 1:1$) to 20 bar and the temperature was raised to 80°C in approximately 1 h. Subsequently, oct-1-ene (20 mmol, 3.14 ml) and decane (3 mmol, 0.6 ml), as internal standard, was added under pressure. A small sample was taken after 20 min (at about 21% conver-

sion), and analyzed by GC. Next, the content was siphoned into a separator funnel containing an aqueous H_2SO_4-solution of pH 1.8 (25 ml). The autoclave was washed twice with 5 ml of toluene. The combined toluene phases and the aqueous phase were thoroughly shaken. After phase separation the colourless toluene layer, containing the decane, oct-1-ene and aldehydes, was washed with a smaller portion of the H_2SO_4-solution. The final pH of the combined, bright yellow aqueous layer was about 2.5, at which pH the free ligand is quantitatively extracted (see Fig. 4). The aqueous layer was then poured into a Schlenk flask and fresh toluene (20 ml) was added. The acidic solution was neutralised to pH 7–8 (1–2 ml) with saturated aqueous $NaHCO_3$-solution, under vigorous stirring. The toluene layer turned brownish–yellow while the resulting aqueous layer turned colourless and became very turbid which did not alter after a subsequent extraction of toluene (10 ml). The combined orange–yellow toluene phases were concentrated to 16 ml. The autoclave was washed with another 20 ml of toluene before it was filled with the recycled reaction mixture and pressurised again to 20 bar syngas at 80°C in 1 h. Oct-1-ene was added and samples were taken when approximately the same conversion was reached as in the first run, as judged from the pressure drop.

In the procedure for a multiple extraction experiment (entry 7, Table 2) the reaction mixture was extracted after catalysis (and cooling with ice below 10°C) by 6 subsequent portions of an aqueous H_2SO_4-solution of pH 2.2 of 15, 2×10 and 3×5 ml, respectively. In the neutralisation step a small amount (about 0.35 ml) of the saturated aqueous $NaHCO_3$-solution was added in the presence of toluene. After removal of the toluene, fresh toluene was added together with a small amount of base (0.25 ml). Thus, the aqueous layer was extracted by 6 portions of toluene of respectively 20, 15, 2×10 and 2×5 ml while the pH never exceeded 7.

Experimental details concerning the rhodium analysis by ICP–AES are given elsewhere [31].

4.3. NMR / IR-experiments

A small vessel was filled with $Rh(acac)(CO)_2$ (0.070 mmol, 18 mg), ligand (0.72 mmol, 0.31 g), oct-1-ene (3.8 mmol, 0.6 ml) and toluene (4 ml), and placed in the autoclave. After 1 h under 20 bar syngas at 80°C, the reaction mixture was siphoned into a flask. It was extracted into D_2O by titration with H_2SO_4 (pH 1) and neutralised with $NaHCO_3$ in the presence of d_8-toluene. All layers were subjected to NMR- and IR-analysis.

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