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A novel dicationic phenoxaphosphino-modified Xantphos-type ligand: a ligand for highly active and selective, biphasic, rhodium catalysed hydroformylation in ionic liquids

Raymond P. J. Bronger,[a] Silvana M. Silva,[b] Paul C. J. Kamer[a] and Piet W. N. M. van Leeuwen*[a]

[a] *van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. E-mail: pwnm@science.uva.nl; Fax: +(31)(0)20-5255604*

[b] *Laboratory of Molecular Catalysis, Instituto de Quimica, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre, 91501-970 RS, Brazil*

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A highly active and regioselective catalyst obtained from a novel dicationic ligand (**1**) and $Rh(CO)_2(acac)$ for hydroformylation of 1-hexene and 1-octene in ionic liquids is reported. Optimisation studies of various reaction parameters led to an unprecedentedly active (TOFs > 6200 mol mol^{-1} h^{-1}, T = 100 °C), selective (l/b ratios > 40) and stable hydroformylation procedure. No catalyst leaching (Rh-loss < 0.07% of initial rhodium intake, P-loss < 0.4% of the initial phosphorus intake) or losses in performance could be measured during 1-octene hydroformylation recycle experiments in 1-butyl-3-methylimidazolium hexafluorophosphate. At low catalyst loadings activities and regioselectivities competitive with one-phase catalysis in conventional solvents were observed. At high catalyst loadings the system is extremely stable and has a long shelf-life as a result of the formation of stable, if inactive rhodium dimers.

Introduction

In recent years much effort has been devoted to the development of catalytic systems that allow facile separation of the products and catalysts.[1] Especially systems that enable efficient catalyst recycling have attracted much attention.[2] In this field the immobilisation of tailor-made catalysts to organic and inorganic solid supports has been successful, but in these systems immobilisation often results in lower catalytic activity due to mass transfer limitations.[3–7] The use of soluble supports, such as dendrimers, results in immobilised homogeneous catalysts that do not suffer from mass transfer limitations,[8–11] but the limited availability of proper membrane material hampers efficient recycling. In recent years room-temperature ionic liquids (RTIL) have proven to be attractive and alternative mediums for many homogeneously catalysed reactions. The properties of ionic liquids can be tuned easily by adjustment of the cation–anion pair. For example, a plethora of imidazolium ionic liquids can be prepared by varying the anion (X^-, PF_6^-, BF_4^-, CH_3COO^-, *etc*...) and the alkyl groups on the aromatic ring. The combination of high density, high stability, non-measurable vapour pressure, and the possibilities for catalyst immobilisation *via* ionic interactions allows easy separation of the catalyst by simple phase separation or distillation and recycling, as most products are not or only slightly soluble in the ionic phase. Comprehensive information on this field can be found in the reviews that have appeared on this subject.[12–16] Compared to the aqueous two-phase catalysis concept,[17,18] the scope of two-phase catalysis can be extended to substrates that are poorly soluble or insoluble in aqueous media. In addition, the use of phosphites,[19] phosphonites and phosphinites as modifying ligands for two-phase catalysis comes within reach in RTILs because degradation reactions, such as hydrolysis,[20,21] are less likely to occur.

For hydroformylation reactions 1-butyl-3-methylimidazolium hexafluorophosphate ($BMI.PF_6$) is often used as the reaction medium. In this medium a good activity,[19,22,23] selectivity[19,22,24] and complete retention of the catalyst[24] can be obtained. Unfortunately, no systems have been reported that combine all three aspects. In order to obtain a catalytic system that combines a high activity, high selectivity and a good retention, we designed a novel diphosphine ligand. Our recent studies have shown that various xanthene based diphosphines show a moderate activity, but a high selectivity in rhodium catalysed hydroformylation.[25–27] This high selectivity is in part retained when modified for use in RTILs.[24,28] In addition, the nature of the anions and cations of both the ionic liquid and the ligand have a major influence on the recyclability of the catalyst. Excellent retention of the catalyst was observed by adjusting the ligand structure to the ions of the solvent.[19] Previously, we had found that when phenoxaphosphino-modified xanthene-type ligands (Fig. 1) are used in conventional solvents the catalytic activity is enhanced considerably.[29,30]

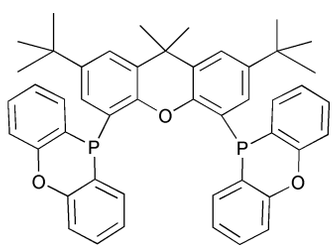

Fig. 1 POP-Xantphos.[29,30]

Here we report our recent advances in the application of a novel phenoxaphosphino-modified Xantphos-type ligand in RTILs (Fig. 2), which was recently reported in a communication.[31]

Results and discussion

Synthesis

Previous studies employing phenoxaphosphino-modified Xantphos-type ligands in the rhodium catalysed hydroformylation in toluene have shown that these systems lead to very high hydroformylation activities and selectivities. Averaged turn-over-frequencies (TOFs) of 1700 mol mol^{-1} h^{-1} (T = 80 °C, $p(CO–H_2, 1:1)$ = 20 bar, [Rh] = 1 mM, [1-octene] = 637 mM) have been observed.[29,30,32,33]

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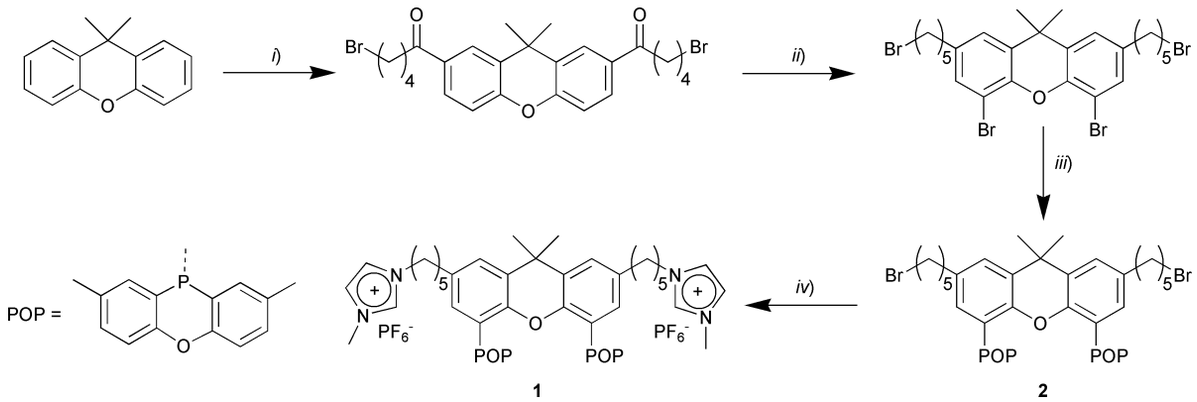


Scheme 1 Synthesis of ligand **1** (yields in parenthesis). Reagents and conditions: (*i*) 2.2 eq. $AlCl_3$/2.2 eq. 5-bromovaleric chloride (90%); (*ii*) (a) $InCl_3$/chlorodimethylsilane (86%), (b) Br_2 (90%); (*iii*) (a) *n*-BuLi, −80 °C, 30 min, (b) 10-chloro-2,8-dimethylphenoxaphosphine (48%); (*iv*) (a) 1-methylimidazole, 80 °C, 8 days in CH_3CN–toluene (46%), (b) KPF_6 in H_2O (77%).

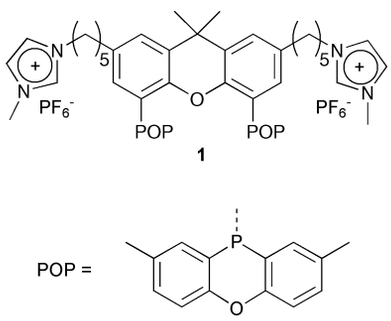


Fig. 2 Novel dicationic ligand.

The high regioselectivity is mainly determined by the differences in the rates of β-hydrogen elimination between the respective rhodium–alkyl species rather than by preferential formation of *linear* alkyl rhodium intermediates.[29,33] The use of this type of ligands for immobilisation procedures results in a relatively high activity compared to other reported systems, while the regioselectivity remains unequivocally high.[31] Studies on related ligands have shown that modification of the 9,9-dimethylxanthene backbone at the 2- and 7-positions with different aliphatic groups does not have a large influence on the catalytic reaction. This is in contrast to modification of the phenoxaphosphino-moieties, which often leads to a change in selectivity.[32] Therefore, a synthetic procedure was developed that allows easy modification of the 9,9-dimethylxanthene backbone by two cationic moieties at the 2- and 7-positions.

Ligand **1** was prepared *via* a six-step synthetic route. The first step involved a Friedel–Crafts acylation using 5-bromovaleryl chloride and 9,9-dimethylxanthene. Next, the ketone functionalities were reduced catalytically using $InCl_3$ and chlorodimethylsilane.[34] Compared to standard methods for reduction, like the Wolff–Kischner or Clemmensen reduction, the catalytic reduction provides a more efficient route. Next, bromination of the 4,5-positions of the modified-xanthene backbone followed by dilithiation and reaction with 10-chloro-2,8-dimethylphenoxaphosphine yielded **2**. Reaction of **2** with two equivalents of 1-methylimidazole at 80 °C followed by a halide/PF_6^- exchange gives the desired ligand **1** in a moderate overall yield (Scheme 1).

Catalysis

The immobilised catalyst precursor was formed by mixing $Rh(CO)_2(acac)$ and four equivalents of ligand in an acetonitrile–BMI.PF_6 mixture. After stirring for 1 h the acetonitrile was removed by evaporation under reduced pressure at 60 °C for 3 h, which afforded a red solution of the ionic liquid catalyst-precursor. Prior to hydroformylation the catalyst precursor was heated at 80 °C for 1 h under 15 bar of CO–H_2 (1 : 1) to start formation of the active hydroformylation catalyst.

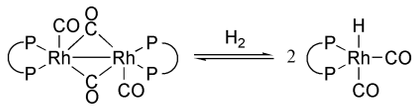
Table 1 Hydroformylation of 1-octene[a]

Cycle	TOF[b,c]	% Isom.[b,d](%)	Sel.[b,e](%)	l/b Ratio[b]
1	65	11.8	86.2	44
2	88	8.3	89.8	49
3	93	7.8	90.1	44
4	112	7.7	90.3	44
5	107	9.6	88.1	38
6[f]	318	13.3	85.0	49
7[f]	305	17.7	80.8	55

[a] Conditions: T = 100 °C, p(CO–H_2, 1 : 1) = 17 bar, [Rh] = 6.4 mM, [**1**] = 27 mM, substrate/Rh = 988, ionic liquid = BMI.PF_6. Rate of stirring = 900 rpm. In none of the experiments was hydrogenation observed. [b] Linear to branched ratio, percent isomerisation to 2-octene, percent linear aldehyde and turnover frequency were determined at ~30% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] % Isom. = (octenes other than 1-octene)/(octenes other than 1-octene + aldehydes) × 100%. [e] Sel. = (linear aldehyde)/(branched aldehyde + octenes other than 1-octene) × 100%. [f] $p(H_2)$ = 40 bar, p(CO) = 6 bar.

Hydroformylation of 1-octene was carried out at 100 °C under 17 bar of CO–H_2 (1 : 1) using 3 mL of ionic liquid and 3 mL of 1-octene. At approximately 30% conversion the reaction was stopped by cooling the autoclave in an ice-bath and venting the gasses. Reactions were run at fairly low conversion in order to calculate the initial activity. Additionally, loss in activity due to catalyst leaching is easier to detect compared to experiments run at full conversion. Recycling experiments were performed by removal of the octene/aldehyde layer by decantation followed by charging the autoclave with 1-octene, repressurisation and heating to the desired temperature. The results of seven consecutive recycling experiments are shown in Table 1.[31]

The applied L/Rh ratio, preparation of catalyst precursor and catalysis conditions are similar to the optimised conditions described by Dupont *et al.* who used sulfonated Xantphos as modifying ligand.[28] Already from the first experiment it is evident that very high linear to branched (l/b) ratios are obtained by employing this ligand, albeit with moderate activity. The increase in catalytic activity observed for recycle experiments (entries 2–4) indicates that probably no complete conversion toward the active rhodium–hydride species had been reached in the first run, an effect also observed by others.[24] Starting from recycle experiment 4 reproducible activities were obtained. The relatively low activity for this ligand system and the red colour of the rhodium complex in the ionic liquid after catalysis suggests the presence of a dimeric rhodium species (Scheme 2).[35] Dimer formation is a known cause for lower activity of rhodium hydroformylation catalysts. As a result the concentration of the active monomeric catalyst species decreases. Since most hydroformylation catalysts exhibit a first order dependency in the concentration of this rhodium–hydride



Scheme 2 Equilibrium between Rh-dimer and Rh–hydride species.

species,[36] the reaction becomes slower. In order to shift the equilibrium between the rhodium monomer and the rhodium dimer towards the rhodium monomer a higher partial hydrogen pressure was applied.[35]

Indeed, the catalytic activity could be enhanced to TOFs > 300 mol mol^{-1} h^{-1} by applying higher hydrogen pressures while keeping the CO pressure constant (Table 1, entries 6 and 7). In addition, even at these high hydrogen pressures, no hydrogenation takes place. Unfortunately, and in contrast to our previous studies using sulfonated Xantphos, no conclusive high-pressure IR and high-pressure NMR data could be obtained for this system.[37] According to ICP analysis of the octene–aldehyde mixture after catalysis neither phosphorus (<100 ppb; <0.4% of the initial phosphorus intake) nor rhodium (<5 ppb; <0.07% of the initial rhodium intake) leaching was detected. Furthermore, the catalyst proved to be extremely stable even under atmospheric conditions without special precautions. When the hydroformylation of 1-octene was repeated after the ionic liquid containing the catalyst had been stored for 14 days at room temperature under air, similar catalysis results were obtained as in the initial hydroformylation experiment, although a slightly higher rate of isomerisation was observed. The increased isomerisation might be due to formation of acidic impurities caused by some anion hydrolysis with moisture from air.[38–41]

The effect of catalyst concentration on hydroformylation

Despite the promising initial results with this catalytic system, the activity is still low compared to catalysis under one-phase conditions, which was conducted at *lower* temperatures.[29,30,32,33] The existence of dimeric rhodium species, possibly still present at high hydrogen pressures, is considered to be the main reason for the relatively low activity. High catalyst concentrations may favour the formation of rhodium dimers[35] and therefore we opted to reduce the catalyst concentration. This was expected to shift the rhodium dimer/monomer equilibrium toward the monomeric rhodium species, but it also reduces the effect of potential mass transfer limitations that are commonly observed for immobilised systems. The results of catalysis at lowered rhodium concentration ([Rh] = 1.7 mM in ionic liquid, [**1**] = 27 mM) and at different stirring rates (from 230 to 1600 rpm) are summarised in Table 2.

Lowering the rhodium concentration results in a tremendous increase in activity per rhodium and in a slight increase in regioselectivity. The effect of stirring rate indicates that we are operating under mass transfer limitations as the activity increases when the reaction mixture is stirred more vigorously. The stirring rate also has a large impact on isomerisation activity, possibly due to differences in dissolution rates of the substrates. Overall the best performance was obtained at a stirring rate of 900 rpm as a good balance between isomerisation and hydroformylation activity was found.

Next, the effect of reducing the ligand concentration was studied ([Rh] = 1.7 mM in ionic liquid, [**1**] = 7 mM) (Table 3). At this lowered ligand concentration slightly higher activities (TOF = 6200 mol mol^{-1} h^{-1}.) were obtained, while maintaining a high l/b ratio. Reducing the p(CO–H_2, 1 : 9) = 60 bar to p(CO–H_2, 1 : 1) = 12 bar resulted in a slight drop in catalytic activity only. This indicates that still some rhodium dimer species might be present under lowered hydrogen pressures, but that the equilibrium is shifted almost completely to the monomeric rhodium species. In addition, the colour of the ionic liquid solution turns yellow instead of remaining red during recycling experiments, supporting this hypothesis.

Table 2 Hydroformylation of 1-octene at different rates of stirring[a]

Cycle	rpm	TOF[b,c]	% Isom.[b,d](%)	Sel.[b,e](%)	l/b ratio[b]
1	550	3450	14	84	64
4–5	230	2900	14	84	63
2–3	550	4850	11	87	65
6–7	900	5150	11	87	59
10–11	1285	6400	19	79	56
8–9	1600	7400	21	77	52

[a] Conditions: T = 100 °C, p(CO–H_2, 1 : 9) = 60 bar, [Rh] = 1.7 mM, [ligand] = 27 mM, substrate/Rh = 3823, ionic liquid = BMI.PF_6. In none of the experiments was hydrogenation observed. [b] Linear to branched ratio, percent isomerisation to 2-octene, percent linear aldehyde and turnover frequency were determined at ~40% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] % Isom. = (octenes other than 1-octene)/(octenes other than 1-octene + aldehydes) × 100%. [e] Sel. = (linear aldehyde)/(branched aldehyde + octenes other than 1-octene) × 100%.

Alternatively, there could exist a small positive order in hydrogen pressure. Decomposition of the catalytic system could be excluded since under the standard reaction conditions the same activity and selectivity were measured, and no rhodium or phosphorus leaching was detected (Table 3, cycle 8).

The very high hydroformylation and isomerisation activity prompted us to test the catalyst for the selective hydroformylation of *trans*-2-octene to nonanal. In order to enhance the isomerisation activity and to suppress the hydroformylation of internal alkenes to branched aldehydes the reaction temperature was increased to 120 °C and the CO pressure was reduced to 2.5 bar (p(CO) = 2.5 bar, p(H_2) = 47.5 bar). Severe catalyst deterioration was observed under these conditions during the hydroformylation of *trans*-2-octene, even at high ligand concentrations ([**1**] = 27 mM). Therefore we also tested the system under identical conditions as for the hydroformylation of 1-octene (Table 3, cycle 9 and 10). High activities but very low l/b ratios were observed, but again the catalyst was not stable when *trans*-2-octene was used as substrate. Subsequent experiments using 1-octene confirmed that catalyst decomposition had taken place (Table 3, cycles 11–13). Why the use of *trans*-2-octene results in catalyst decomposition is currently unclear, as the resting state is most likely the species (diphosphine)-$RhH(CO)_2$ for both 1-octene and *trans*-2-octene hydroformylation.[42] Perhaps unidentified impurities are present in *trans*-2-octene, such as dienes and enones.[43] The low rate of alkene coordination is determined by the lower reactivity of internal alkenes and the low concentration of the alkene in the ionic liquid. Rhodium and phosphorus leaching was detected (1% Rh and 8% P leaching of the initial intake). The low selectivity and increased activity of experiments 11–13 compared to recycle experiments 1–8 are typical of non-ligated rhodium, which could point to ligand decomposition.

Remarkably, a stable catalyst system under ambient conditions is only obtained at high catalyst loadings, because at low concentrations decomposition is observed within a few days after exposing the catalyst to air. When stored under a pressure of CO/H_2 the catalyst retains its activity and selectivity. Apparently, only the rhodium-dimer is stable under ambient conditions.

Overall the activity and selectivity for the 1-octene hydroformylation experiments are by far superior to those reported by others under comparable reaction conditions (Table 4).

Hydroformylation of 1-octene and 1-hexene at 80 °C and hydroformylation in HMI.PF_6

Hydroformylation at 80 °C was carried out to enable a valid comparison with literature data on the one-phase systems (Table 5). At this temperature TOFs of 1200 mol mol^{-1} h^{-1} were

Table 3 Hydroformylation of 1-octene and *trans*-2-octene[a]

Cycle	Substrate	TOF[b,c]	% Isom.[b,d](%)	Sel.[b,e](%)	l/b Ratio[b]
1	1-Octene	5250	26.5	72	45
2	1-Octene	6150	23.6	75	41
3	1-Octene	6800	21.0	77	43
4	1-Octene	7200	21.3	77	43
5	1-Octene	6650	27.0	71	42
6[f]	1-Octene	5100	15.8	82	44
7[f]	1-Octene	5000	13.4	85	41
8	1-Octene	6650	26.6	72	41
9	*trans*-2-Octene	1200	13.6[g]	37	0.7[h]
10	*trans*-2-Octene	1200	16.3[g]	14	0.2[h]
11	1-Octene	9600	nd[i]	Nd	1.9
12	1-Octene	10100	23.0	54	2.4
13	1-Octene	8700	26.0	53	2.5

[a] Conditions: T = 100 °C, p(CO–H_2, 1 : 9) = 60 bar, [Rh] = 1.7 mM, [ligand] = 7 mM, substrate/Rh = 3823, ionic liquid = BMI.PF_6. Rate of stirring = 900 rpm. In none of the experiments was hydrogenation observed. [b] Linear to branched ratio, percent isomerisation to 2-octene, percent linear aldehyde and turnover frequency were determined at ~40% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] % Isom. = (octenes other than 1-octene)/(octenes other than 1-octene + aldehydes) × 100%. [e] Sel. = (linear aldehyde)/(branched aldehyde + octenes other than 1-octene) × 100%. [f] p(CO–H_2, 1 : 1) = 12 bar. [g] Predominantly isomerisation to *cis*-2-octene. [h] The differences in l/b ratio between cycle 9 and cycle 10 are most likely caused by some aldehydes present in the RTIL from the previous catalysis experiment (cycle 8). [i] nd = Not determined.

Table 4 Comparison of different systems[a]

Ligand backbone	Ref.	TOF[b]	Rate[c]	l/b Ratio	Rh leaching[d](%)	P leaching[d](%)
Phenol[e,f]	19	240	1.3	13	2	nr[g]
2-Imidazolium[h]	23	552	1.3	1	nr	nr
Cobaltocenium[i]	22	810	2.0	16	<0.2	nr
Xanthene[j]	24	52	nd[k]	21	<0.07[l]	nr
Xanthene[m]	28	32	0.1	13	nr	nr
Xanthene[i]	This work	**6200**	**5.3**	**44**	<0.07[l]	<0.4[j]

[a] Conditions: T = 100 °C, p(CO–H_2) = 10–60 bar, substrate = 1-octene, ionic liquid = BMI.PF_6. In none of the experiments was hydrogenation observed. [b] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [c] Rate = (mol aldehyde) L^{-1} h^{-1}. [d] Percentage of leached rhodium/phosphorus of initial intake. [e] Monophosphite ligand. [f] Substrate = 1-hexene, T = 80 °C. [g] nr = Not reported. [h] Monophosphine ligand. [i] Diphosphine ligand. [j] Phenylguanidium modified diphosphine ligand. [k] nd = No sufficient data to calculate the rate in (mol aldehyde) L^{-1} h^{-1}. [l] Detection limit of ICP analysis. [m] Sulfonated diphosphine ligand.

Table 5 Hydroformylation of 1-hexene and 1-octene[a]

Cycle	Substrate	T/°C	TOF[b,c]	% Isom.[b,d](%)	Sel.[b,e](%)	l/b Ratio[b]
1	1-Octene	100	4800	12.3	86	45
2	1-Octene	100	6250	11.1	87	42
3	1-Octene	100	6200	13.0	85	44
4–6	1-Octene	80	1200	10.3	88	50
7[f,g]	1-Hexene	80	4000	nd	nd	54
8[f,g]	1-Hexene	80	5800	nd	nd	58
9[f,g]	1-Hexene	80	8900	nd	nd	54
10–15	1-Octene	80	950	12.2	85	31

[a] Conditions: T = 100 °C, p(CO–H_2, 1 : 9) = 60 bar, [Rh] = 1.7 mM, [ligand] = 7 mM, substrate/Rh = 3823, ionic liquid = BMI.PF_6. Rate of stirring = 900 rpm. In none of the experiments was hydrogenation observed. [b] Linear to branched ratio, percent isomerisation to 2-octene, percent linear aldehyde and turnover frequency were determined at ~40% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] % Isom. = (octenes other than 1-octene)/(octenes other than 1-octene + aldehydes) × 100%. [e] Sel. = (linear aldehyde)/(branched aldehyde + octenes other than 1-octene) × 100%. [f] Substrate/Rh = 4821. [g] Cycle 7: 89% conversion, cycle 8: 77% conversion, cycle 9: 49% conversion.

observed; these surprisingly high activities are competitive with results obtained under typical one-phase hydroformylation conditions (TOF = 1700 mol mol^{-1} h^{-1}, solvent = toluene, T = 80 °C, p(CO–H_2, 1 : 1) = 20 bar, [Rh] = 1 mM, [1-octene] = 637 mM).[29,30,32,33] To investigate the influence of substrate solubility 1-hexene was tested as substrate in BMI.PF_6, because the solubility of 1-hexene in BMI.PF_6 is higher than that of 1-octene. Under one-phase conditions, the hydroformylation of 1-hexene or 1-octene gives similar results as regards both activity and selectivity.[33,44] Differences in performance between the two substrates in ionic liquids might be attributed to differences in solubility, but the activation parameters of the two processes for the two substrates have not been determined. Comparison of the results shows that a much higher activity for the hydroformylation of 1-hexene is obtained (Table 5).

The use of 1-hexene leads to 8% rhodium leaching, determined by ICP analysis, after three recycle experiments. The large increase in TOF that is observed from cycle 7–9 can therefore in part be attributed to catalysis not taking place in the ionic liquid phase, but in the substrate phase. Leaching was corroborated by consecutive hydroformylation reactions with 1-octene at T = 80 °C since the TOF dropped from 1200 mol mol^{-1} h^{-1} for the initial hydroformylation experiments (cycle 4–6) to 950 mol mol^{-1} h^{-1} for the experiments performed after 1-hexene hydroformylation (cycle 10–15). This loss in activity (21%) is larger than the detected loss of rhodium (8%), which might indicate catalyst decomposition. Catalyst decomposition would also explain the loss in regioselectivity. During none of the 1-octene hydroformylation experiments rhodium or phosphorus leaching was detected.

Table 6 Hydroformylation of 1-octene in $HMI.PF_6$[a]

Cycle	TOF[b,c]	% Isom.[b,d](%)	Sel.[b,e](%)	l/b Ratio[b]
1	1400	10.8	87	41
2	4950	5.9	92	44
3–6	9000	16.6	81	44
7–9[f]	5250	19.0	79	43

[a] Conditions: T = 100 °C, $p(CO–H_2, 1:9)$ = 60 bar, [Rh] = 1.7 mM, [ligand] = 7 mM, substrate/Rh = 3823, ionic liquid = $HMI.PF_6$. Rate of stirring = 900 rpm. In none of the experiments was hydrogenation observed. [b] Linear over branched ratio, percent isomerisation to 2-octene, percent linear aldehyde and turnover frequency were determined at ~40% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] % Isom. = (octenes other than 1-octene)/(octenes other than 1-octene + aldehydes) × 100%. [e] Sel. = (linear aldehyde)/(branched aldehyde + octenes other than 1-octene) × 100%. [f] $p(CO–H_2, 1:1)$ = 12 bar.

The cause of this different behaviour of the catalyst system when using different substrates is unclear, therefore 1-hexyl-3-methylimidazolium hexafluorophosphate ($HMI.PF_6$) was used as the reaction medium as the solubility of 1-octene is increased in this solvent.[15,40] The results for the recycling experiments are summarised in Table 6.

The activity for 1-octene hydroformylation increases from TOFs of ~6200 mol mol^{-1} h^{-1} in $BMI.PF_6$ to TOFs of ~9000 mol mol^{-1} h^{-1} in $HMI.PF_6$, while maintaining a high l/b ratio. The catalyst can again be recycled for at least 10 times without showing any noticeable loss in activity or selectivity, but in contrast to the recycle experiments in $BMI.PF_6$ detectable rhodium leaching occurs, albeit in trace amounts (0.07–0.08% of the initial rhodium intake). Surprisingly, only minor differences in activity between catalysis in $BMI.PF_6$ or $HMI.PF_6$ are measured when the pressure is reduced to 12 bar of $CO–H_2$ (1 : 1). Although the differences in catalysis could be ascribed to differences in substrate solubility, it must be noted that other minor differences between the two ionic liquids exists that influence catalysis, like viscosity and surface tension, as both parameters affect the rates of mass transfer.[39] Also differences in dissolution rates of CO and H_2 influence the catalysis results, as corroborated by the effect of stirring rate on activity.

From a thermodynamic point-of-view the differences in catalysis results between the two ionic liquids are not clear. If the three phases of the reaction mixtures are in equilibrium than the chemical potential of the gas-phase, substrate-phase and ionic liquid-phase should be equal. For the experiments with $BMI.PF_6$ and $HMI.PF_6$ the same CO and H_2 pressures were applied, the ionic liquids have no measurable vapour pressure, and therefore the vapour pressure of the substrate should be equal and independent of the ionic liquid. Consequently, the activity (or fugacity) of CO, H_2 and substrate should be irrespective of the ionic liquid employed, and the catalytic activities should be the same if the activation parameters of the reaction were the same. Since the rates are not the same, more research is required to elucidate the exact thermodynamic parameters of all mixtures. The first results seem to suggest that above 900 rpm no mass-transfer limitations are involved, but this needs further scrutiny for all substrates and conditions.

Conclusions

A synthetic route toward a novel functionalised phenoxaphosphino-modified ligand has been described. While this ligand was specifically designed for use in ionic liquids, minor adjustments of the synthetic procedure will allow easy modification of the ligand with other functional groups. During recycling experiments under different reaction conditions we have shown that the efficiency of this catalyst system is sensitive to the catalyst concentration, partial hydrogen pressure, stirring rate, substrates and ionic liquids employed. The best results were obtained by using a low rhodium concentration, a high hydrogen pressure and a stirring rate of 900 rpm in $BMI.PF_6$ as the ionic liquid and 1-octene as the substrate. Under these conditions an unrivalled combination of activity, regioselectivity and recyclability has been observed in the rhodium catalysed hydroformylation of 1-octene in ionic liquids.

Experimental

General procedures

All air- or water-sensitive reactions were performed using standard Schlenk techniques under an atmosphere of purified argon. Toluene was distilled from sodium, THF from sodium/benzophenone, and hexanes from sodium/benzophenone/triglyme. Isopropanol and dichloromethane were distilled from CaH_2. Chemicals were purchased from Acros Chimica, and Aldrich Chemical Co. Silica gel 60 (230–400 mesh) purchased from Merck was used for column chromatography. 1-*n*-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid ($BMI.PF_6$)[45] and 2,8-dimethyl-10-chlorophenoxaphosphine[46] were prepared according to literature procedures. It is important to note that the quality of the ionic liquid has a large impact on the percentage of isomerisation (compare the results of Tables 3 and 5). Traces of water in the ionic liquid might lead to some anion hydrolysis, which might cause a higher proportion of isomerisation. However, reactions with the same ionic liquid give reproducible results; laboratory-prepared ionic liquid led to a lower percentage of isomerisation than the commercially available ionic liquid.

Melting points were determined on a Gallenkamp MFB-595 melting point apparatus in open capillaries and are reported uncorrected. NMR spectra were recorded on a Varian Mercury 300 and Inova 500 spectrometer. ^{31}P and ^{13}C spectra were measured in ^{1}H decoupled mode. TMS was used as an external standard for ^{1}H and ^{13}C NMR and 85% H_3PO_4 in H_2O as an external standard for ^{31}P NMR. Hydroformylation reactions were carried out in a 75 mL home-made stainless steel autoclave. The alkene was purified by percolation over neutral activated alumina. The reactions were terminated by cooling on ice, stopping the mechanical stirring and by venting the gases. Synthesis gas ($CO–H_2$, 1 : 1, 99.9%), CO and H_2 were purchased from Air Liquide. Gas chromatographic analyses were run on an Interscience HR GC Mega 2 apparatus (split/splitless injector, J&W Scientific, DB-1 30 m column, film thickness 3.0 mm, carrier gas 70 kPa He, FID detector) equipped with a Hewlett Packard Data system (Chrom-Card).

2,7-Di(5-bromopentanoyl)-9,9-dimethylxanthene. At 0 °C 24.9 g of $AlCl_3$ (187 mmol) was added slowly to a stirred solution of 17 g of 9,9-dimethylxanthene (81 mmol) and 25 mL of 5-bromovaleric chloride (187 mmol; 2.3 equivalents) in 250 mL of CH_2Cl_2. After overnight stirring the reaction mixture was poured into 100 mL of ice–water and extracted with CH_2Cl_2 (3 × 100 mL). Subsequently, the organic layer was dried over $MgSO_4$. The solvents were removed *in vacuo* and the resulting dark green solid was purified by flash column chromatography over silica (eluent: CH_2Cl_2). Yield: 39 g of a yellow–green solid (90%) that was used without further purification. ^{1}H NMR ($CDCl_3$): δ 8.10 (d, $^{4}J(H,H)$ = 1.8 Hz, 2H), 7.83 (dd, $^{3}J(H,H)$ = 8.7 Hz, $^{4}J(H,H)$ = 2.1 Hz, 2H), 7.12 (d, $^{3}J(H,H)$ = 8.4 Hz, 2H), 3.46 (t, $^{3}J(H,H)$ = 6.6 Hz, 4H), 3.00 (t, $^{3}J(H,H)$ = 6.9 Hz), 1.93 (m, 8H), 1.70 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 198.41 (s), 153.49 (s), 132.96 (s), 130.10 (s), 128.40 (s), 127.38 (s), 116.90 (s), 37.46 (s), 34.95 (s), 34.35 (s), 33.32 (s), 33.11 (s), 23.09 (s).

2,7-Di(5-bromopentyl)-9,9-dimethylxanthene. To a stirred suspension of 1.3 g $InCl_3$ (5.9 mmol) and 27.6 mL of chloro-

dimethylsilane (4.8 eq., 245 mmol) in 80 mL of CH_2Cl_2 was added 27.2 g of 2,7-di-5-bromopentan-1-one-9,9-dimethylxanthene (51 mmol) in 80 mL of CH_2Cl_2. The reaction was followed by GC-MS and IR and quenched by addition of 100 mL of water after complete reduction of the ketone functionalities (~4 h reaction time). Next, the mixture is extracted with 3 × 80 mL of CH_2Cl_2. Subsequently, the organic layer was dried over $MgSO_4$. The solvents were removed *in vacuo* and the resulting solid was purified by flash column chromatography (eluent: hexanes). Yield: 22 g of a slightly yellow compound (86%) that was used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.18 (d, ^4J(H,H) = 1.8 Hz, 2H), 6.99 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.1 Hz, 2H), 6.94 (d, ^3J(H,H) = 7.8 Hz, 2H), 3.41 (t, ^3J(H,H) = 6.6 Hz, 4H), 2.60 (t, ^3J(H,H) = 7.8 Hz, 4H), 1.89 (m, 4H), 1.66 (m, 4H), 1.61 (s, 6H), 1.49 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.96 (s), 136.91 (s), 129.98 (s), 127.49 (s), 126.09 (s), 116.36 (s), 35.58 (s), 34.24 (s), 34.19 (s), 32.94 (s), 32.67 (s), 31.13 (s), 28.08 (s). GC-MS (*m*/*z*, rel. intensity): 508 (M^+, 8), 493 (100), 413 (20), 371 (9), 356 (14), 276 (14), 221 (22), 207 (27), 131 (18), 55 (22).

4,5-Dibromo-2,7-di(5-bromopentyl)-9,9-dimethylxanthene. To an ice-cooled solution of 13.5 g of 2,7-di-5-bromopentyl-9,9-dimethylxanthene (26.6 mmol) in 130 mL of CH_2Cl_2 was added dropwise 4.9 mL of Br_2 (3.6 eq., 95.0 mmol) in 4.9 mL of hexane. The reaction mixture was warmed to room temperature and stirred overnight. Next the excess of Br_2 is quenched with 100 mL of an aqueous $NaSO_3$ solution, and the mixture extracted with 3 × 80 mL of CH_2Cl_2. Subsequently, the organic layer was dried over $MgSO_4$. The solvents were removed *in vacuo* and the resulting solid was purified by flash column chromatography (eluent: CH_2Cl_2). Yield: 15.9 g of a yellow solid (89.6%) that was used without further purification. ^{1}H NMR ($CDCl_3$): δ 7.28 (s, 2H), 7.11 (s, 2H), 3.4 (t, ^3J(H,H) = 6.6 Hz, 4H), 2.57 (t, ^3J(H,H) = 7.5 Hz, 4H), 1.88 (m, 4H), 1.59 (s, 6H), 1.59–1.47 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 145.84 (s), 138.65 (s), 131.80 (s), 131.25 (s), 124.99 (s), 110.88 (s), 35.66 (s), 35.29 (s), 34.09 (s), 32.81 (s), 32.07 (s), 30.84 (s), 27.93 (s).

2,7-Di(5-bromopentyl)-9,9-dimethyl-4,5-di(2,8-dimethyl-10-phenoxaphosphino)xanthene (2). At −78 °C 2.2 mL of *n*-butyllithium (2.5 M in hexanes, 5.5 mmol) was added to a stirred solution of 1.6 g of 4,5-dibromo-2,7-di(5-bromopentyl)-9,9-dimethylxanthene (2.4 mmol). The resulting solution was stirred for 30 min at −78 °C. Subsequently, a suspension of 1.5 g of 2,8-dimethyl-10-chlorophenoxaphosphine (5.7 mmol) in 15 mL of toluene was added dropwise. The reaction mixture was slowly warmed to room temperature and stirred overnight. Next the diethyl ether was removed *in vacuo* and the mixture was diluted with 40 mL of CH_2Cl_2 and hydrolyzed with 10 mL of a 10% aqueous HCl solution. The water layer was removed and the organic layer was dried over $MgSO_4$. The solvents were removed *in vacuo* and the resulting yellow–white solid was crystallized from 2-propanol–toluene. Yield: 1.1 g of white crystals (48%). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −70.51. ^{1}H NMR ($CDCl_3$): δ 7.94 (br d, ^3J(P,H) = 5.5 Hz, 4 H), 7.19 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.5 Hz, 4H), 7.11 (d, ^3J(H,H) = 8.5 Hz, 4H), 7.06 (d, ^4J(H,H) = 1.5 Hz, 2H), 6.51 (d, ^4J(H,H) = 1.5 Hz, 2H), 3.47 (t, ^3J(H,H) = 6.5 Hz, 0.8H; CH_2Cl), 3.45 (t, ^3J(H,H) = 6.5 Hz, 3.2H; CH_2Br), 2.40 (t, ^3J(H,H) = 7.5 Hz, 4H), 2.35 (s, 12H), 1.79 (q, ^3J(H,H) = 7.5 Hz, 4H), 1.54 (s, 6H), 1.43 (m, 4H), 1.32 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.38 (s), 150.88 (t, 10.3 Hz), 136.92 (s), 135.77 (vt, 21.7 Hz), 133.64 (s), 132.91 (t, 5.2 Hz), 131.76 (s), 131.69 (s), 130.05 (s), 127.11 (s), 118.30 (br s), 117.58 (s), 35.10 (s), 34.68 (s), 33.91 (s), 32.83 (s), 32.58 (s), 30.27 (s), 27.66 (s), 20.85 (s). Anal. Calc. for $C_{53}H_{54}Br_2O_3P_2$: C, 66.26; H, 5.67. Found: C, 66.68; H, 5.62%.

2,7-Di(5-(3-methylimidazolium)pentyl)-9,9-dimethyl-4,5-di-(2,8-dimethyl-10-phenoxaphosphino)xanthene hexafluorophosphate (1). To a stirred solution of 490 mg of 2,7-di(5-bromopentyl)-9,9-dimethyl-4,5-bis(2,8-dimethyl-10-phenoxaphosphino)xanthene (0.52 mmol) in 30 mL of an acetonitrile–toluene mixture (1 : 1) was added 0.1 mL of 1-methylimidazole (2.7 eq., 1.4 mmol). The mixture was heated to 80 °C and stirred for 8 days to obtain complete conversion. Next, the solvents were removed *in vacuo* and the resulting solid was purified by precipitation from toluene–acetonitrile. Yield: 250 mg of a white solid (46%). Mp = 216 °C (decomp.). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −69.03. ^{1}H NMR (CD_2Cl_2): δ 10.45 (s, 2H), 7.98 (br d, ^3J(P,H) = 5.4 Hz, 4 H), 7.3–7.1 (m, 14 H), 6.51 (br s, 2H), 4.22 (t, ^3J(H,H) = 7.5 Hz, 4H), 4.01 (s, 3H), 2.40 (m, 4H), 2.36 (s, 12H), 1.84 (q, ^3J(H,H) = 7.5 Hz, 4H), 1.53 (s, 6H), 1.48 (m, 4H), 1.27 (m, 4H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.17 (s), 152.72 (t, 20.5 Hz), 139.17 (s), 137.52 (t, 22.0 Hz), 135.24 (s), 133.83 (s), 133.36 (s), 132.36 (s), 129.33 (s), 128.86 (vt, unresolved), 125.34 (s), 123.83 (s), 120.05 (s), 119.51 (s), 51.87 (s), 38.58 (s), 36.93 (s), 36.64 (s), 34.12 (s), 32.47 (s), 32.07 (s), 27.49 (s), 22.53 (s). To a suspension of 150 mg of 2,7-di(5-(3-methylimidazolium)pentyl)-9,9-dimethyl-4,5-di(2,8-dimethyl-10-phenoxaphosphino)xanthene bromide (0.14 mmol) in H_2O was added 78 mg of KPF_6 (3 eq., 42 mmol). After overnight stirring the solvent is removed *in vacuo* and 15 mL of CH_2Cl_2 was added. After filtration of the salts (KBr) the CH_2Cl_2 is removed *in vacuo* yielding a white powder (yield: 130 mg, 77%). Mp = 221 °C (decomp.). ^{31}P{^{1}H} NMR (CD_3CN): δ 61.42 (heptet, ^1J(P,F; PF_6^-) = 706 Hz), −66.02 (s). ^{19}F{^{1}H} NMR (CD_3CN): δ −67.80 (d, ^1J(P,F) = 704 Hz). ^{1}H NMR (CD_3CN): δ 8.38 (br s, 2H), 7.97 (dd, ^3J(P,H) = 6.6 Hz, ^4J(H,H) = 1.4 Hz, 4H), 7.34 (m, 4H), 7.28 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.1 Hz, 4H), 7.24 (d, ^4J(H,H) = 2H), 7.15 (d, ^3J(H,H) = 8.1 Hz, 4H), 6.45 (d, ^4J(H,H) = 1.5 Hz, 2H), 4.06 (t, ^3J(H,H) = 7.2 Hz, 4H), 3.83 (s, 6H), 2.38 (t, ^3J(H,H) = 7.8 Hz, 4H), 2.36 (s, 6H), 1.76 (m, 4H), 1.51 (s, 6H), 1.42 (m, 4H), 1.21 (m, 4H). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 154.15 (s), 150.45 (t, 22.6 Hz), 137.67, 137.15 (s), 135.49 (t, 21.4 Hz), 133.64 (s), 132.85 (s), 131.21 (s), 130.52 (s), 128.41 (s), 126.73 (vt, unresolved), 124.31 (s), 122.91 (s), 118.21 (s), 117.75 (s), 49.56 (s), 36.09 (s), 34.52 (s), 31.79 (s), 30.38 (s), 29.59 (s), 25.27 (s), 19.95 (s). Anal. Calc. for $C_{61}H_{65}F_{12}N_4O_3P_4$: C, 58.42; H, 5.22; N, 4.47. Found: C, 58.26; H, 5.40; N, 4.58%.

Hydroformylation. The catalyst precursor was prepared by adding 3 mL of BMI.PF_6 to a stirred solution of 1.3 mg of $Rh(CO)_2$(acac) (5 μmol) and 4 equivalents of ligand in 5 mL of acetonitrile. After 1 h the acetonitrile was removed under reduced pressure at 60 °C for 3 h affording a red ionic liquid solution.

In a typical hydroformylation experiment a home-made 75 mL autoclave was charged with this catalyst-precursor containing solution. After purging the autoclave three times with CO–H_2 (1 : 1), the reactor was brought to 5 bar of CO and 45 bar of H_2. Next the autoclave was heated to 80 °C. After 1 h at 80 °C the autoclave was cooled down to room temperature and the gases were vented. The substrate (3 mL) was added and the reactor was pressurised to 5 bar of CO and 45 bar of H_2. Next the autoclave was heated to 100 °C, reaching a total pressure of 60 bar. Reactions were started by stirring at 900 rpm. After 15 min the stirring was stopped and the autoclave was rapidly cooled on ice. After venting the gases, the top layer was removed by decantation. New substrate was added, the reactor was purged, pressurised and heated for the next hydroformylation cycle.

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