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A novel dicationic phenoxaphosphino-modified Xantphos-type ligand—a unique ligand specifically designed for a high activity, selectivity and recyclability†

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A novel phenoxaphosphino-modified ligand has been prepared and successfully employed in the rhodium catalysed hydroformylation of 1-octene in ionic liquids showing unprecedented high selectivity and activity without detectable rhodium or phosphorus leaching during recycling experiments.

In recent years room temperature ionic liquids (RTIL) have proven to be attractive mediums for many homogeneously catalysed reactions. Much attention has been devoted to this chemistry due to the prospects of 'green' catalysis, because easy product and catalyst separation is possible. In many cases the products are slightly soluble in the ionic phase and as a result the catalyst can be separated by simple phase separation and recycled.[1] Compared to the aqueous two-phase catalysis concept, 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,[2] phosphonites and phosphinites as modifying ligands for two-phase catalysis in RTILs comes within reach because degradation reactions, such as hydrolysis,[3] are less likely to occur.

For hydroformylation reactions 1-butyl-3-methylimidazolium hexafluorophosphate ($BMI{\cdot}PF_6$) is often used as reaction medium, usually showing good activity,[2,4,5] selectivity[2,5,6] or complete retention of the catalyst.[6] However, to the best of our knowledge, no RTIL-system for hydroformylation is known that combines all three aspects.

In order to obtain a catalytic system that combines a high activity, high selectivity and a good retention, a novel diphosphine ligand was designed. Recent studies have shown that various xanthene based diphosphines show a relatively high selectivity when modified for use in RTILs.[6,7] For the hydroformylation of 1-octene in conventional solvents like toluene, ligands based on the xanthene(-type) backbone always proved to be very active and selective.[8] Especially when phenoxaphosphino-modified ligands are used the catalytic activity is enhanced considerably.[9] Third, the effect of the nature of the anions and cations of the ionic liquid and ligand has a major influence on the recyclability of the catalyst. Excellent retention of the catalyst was observed by adjusting the ligand to the ions of the solvent.[2] Therefore, we opted to synthesize a phenoxaphosphino-modified xantphos-type ligand that contains two 1-methyl-3-pentylimidazolium hexafluorophosphate moieties (**1**) resembling closely the reaction medium (Fig. 1).

The ligand can easily be prepared *via* a six-step synthetic route. First, a Friedel–Crafts acylation using 5-bromovalericacid chloride and 9,9-dimethylxanthene was carried out. The ketone functionalities were catalytically reduced using $InCl_3$ and chlorodimethylsilane,‡ [10] because standard methods for reduction, like the Wolff-Kischner or Clemmensen reduction, cannot be used due to the reactivity of the bromo-group. Next, bromination on the 4,5 positions of the 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 X^-—PF_6^- (X = halogen) exchange gives the desired ligand **1** (Scheme 1).

The catalyst was immobilised by mixing 5 mg of $Rh(CO)_2(acac)$ and four equivalents of ligand in an acetonitrile/$BMI{\cdot}PF_6$ mixture. After stirring for 1 h the acetonitrile was removed by evaporation under reduced pressure at 60 °C for 3 h affording a red ionic liquid catalyst solution. The hydroformylation of 1-octene was carried out at 100 °C under 17 bar 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 venting the gases and cooling down the autoclave in an ice-bath. Recycling experiments were performed by removal of the octene–aldehyde layer followed by subsequent charging of fresh 1-octene, repressurisation and heating the autoclave to the desired temperature. The results of seven consecutive recycling experiments are shown in Table 1.

The applied catalysis conditions were the same as the optimised conditions described by Dupont *et al.* where sulfonated Xantphos was used as modifying ligand.[7] Already from the first experiment it is clear that very high linear over branched (l/b) ratios are obtained by employing this ligand, albeit with moderate activity. The increase in catalytic activity observed for recycle experiments 2 through to 4 possibly indicate that incomplete conversion to the active rhodium–hydride species has taken place. Others also reported this effect.[6] Only from recycle experiment 4 were stable catalysis results obtained. The relatively low activity for this ligand system and the red color of the rhodium complex in the ionic liquid suggests the presence of a dimeric rhodium species.[11] In order to shift the equilibrium between the rhodium–hydride and the rhodium-dimer towards the rhodium–hydride a higher partial hydrogen pressure was applied (Scheme 2). Indeed, the catalytic activity could be enhanced threefold, to TOFs > 300 h^{-1}, by applying higher pH_2 while keeping the pCO constant (Table 1, entries 6 and 7).

The excellent recycling results were confirmed by ICP analysis of the octene–aldehyde mixture after catalysis. No phosphorus (< 100 ppb) or rhodium (< 5 ppb) leaching was

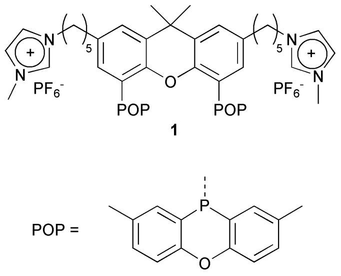

Fig. 1 Novel dicationic ligand.

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b209486j/

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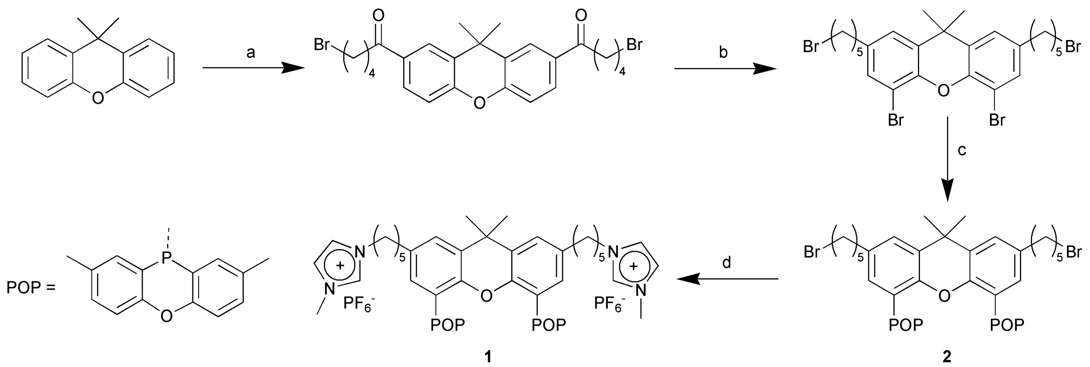
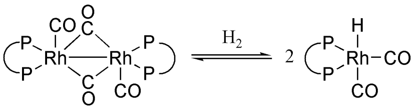


Scheme 1 Synthesis of ligand **1** (yields in parenthesis). *Reagents and conditions*: (a) 2.2 eq. $AlCl_3$/2.2 eq. 5-bromovalericacid chloride (90%), (b) 1) $InCl_3$/ chlorodimethylsilane (86%), 2) Br_2 (90%), (c) 1) *n*-BuLi, −80 °C, 30 min., 2) 10-chloro-2,8-dimethylphenoxaphosphine (48%), (d) 1)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

Table 1 Hydroformylation of 1-octene[a]

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

[a] *Conditions*: T = 100 °C, $p(CO–H_2$, 1:1) = 17 bar, ligand/Rh = 4, substrate/Rh = 988. 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 ~30% alkene conversion. [c] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [d] pH_2 = 40 bar, pCO = 6 bar.



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

detected at all. Furthermore the catalyst proved to be extremely stable even under atmospheric conditions without taking special precautions. Hydroformylation of 1-octene after storing the ionic liquid containing the catalyst at room temperature under air for more than 14 days resulted in equal catalysis results as the previous hydroformylation experiment, although a slightly higher rate of isomerisation is observed. The increased isomerisation might be due to formation of acidic impurities caused by some anion hydrolysis with moisture from air.

Table 2 Comparison of different systems[a]

Ligand backbone	Ref.	TOF[b]/h^{-1}	l/b	Rh leaching[c] (%)	P leaching[c] (%)
Phenol[d]	2[e]	240	13	2	nr[f]
2-Imidazolium[g]	4	552	1	nr	nr
Cobaltocenium[h]	5	810	16	< 0.2	nr
Xanthene[i]	6	52	21	< 0.07[j]	nr
Xanthene[k]	7	32	13	nr	nr
Xanthene	Our system	317	49	< 0.07[j]	< 0.4[j]

[a] *Conditions*: reaction medium = BMI·PF_6, substrate = 1-octene, T = 100 °C, $p(CO–H_2)$ = 10–46 bar. [b] Turnover frequency = (mol aldehyde) (mol Rh)$^{-1}$ h^{-1}. [c] Percentage of leached rhodium/phosphorus of initial intake. [d] Monophosphite ligand. [e] Substrate = 1-hexene, T = 80 °C. [f] nr = Not reported. [g] Monophosphine ligand. [h] Diphosphine ligand. [i] Phenylguanidium modified diphosphine ligand. [j] Detection limit of ICP analysis. [k] Sulfonated diphosphine ligand.

In conclusion, we have reported for the first time, the use of a phenoxaphosphino-modified ligand in RTILs. This novel catalytic system offers a unique combination of a high activity, a high selectivity for the preferred linear aldehyde with complete retention of the catalyst in the ionic phase (see Table 2 for a comparison with some other systems). Besides, the catalyst proved to be stable for more than two weeks under ambient conditions, which shows the high stability of the system. Nevertheless, because of the aforementioned reasons, storage under inert atmosphere is advisable. Further work to improve activity, in order to enable selective hydroformylation of internal olefins, is currently in progress.

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Notes and references

‡ By applying these conditions the bromo-groups were partially substituted by chloro-groups. This substitution is clearly observed in both ^1H NMR and GC–MS spectra. This substitution did not appear to have a negative effect on further reactions, although reaction of 1-methylimidazole with bromoalkyl groups proceeds much faster than reaction with chloroalkyl groups.

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