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Cationic phosphine ligands with phenylguanidinium modified xanthene moieties—a successful concept for highly regioselective, biphasic hydroformylation of oct-1-ene in hexafluorophosphate ionic liquids

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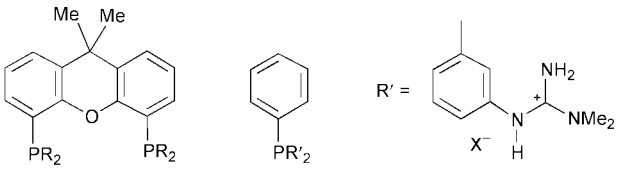
New guanidinium-modified diphosphine ligands with a xanthene backbone show high overall activity and high regioselectivity in the biphasic hydroformylation of oct-1-ene using hexafluorophosphate ionic liquids.

Biphasic catalysis is a well-established method for effective catalyst separation and recycling. In the case of Rh-catalysed hydroformylation reactions this principle is technically realised in the Ruhrchemie–Rhône-Poulenc process where an aqueous catalyst phase is used.[1,2] Unfortunately, this process is limited to C_2–C_5 olefins due to the low water solubility of higher olefins. As an alternative polar medium for biphasic hydroformylation, Chauvin *et al.* suggested novel solvents known as ionic liquids (for general reviews see refs. 3–5). These authors described in detail the biphasic hydroformylation of pent-1-ene with $[Rh(CO)_2acac]$/triarylphosphine in *e.g.* 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$).[6,7] However, none of the tested ligands (PPh_3, sulfonated triaryl phosphines) allowed a combination of high activity, complete retention of the catalyst in the ionic liquid and high selectivity for the desired linear hydroformylation product. Recently, some of us described the successful application of cobaltocenium ligands in the Rh-catalysed hydroformylation of oct-1-ene in hexafluorophosphate ionic liquids, demonstrating that the reaction benefits from the use of ligand systems that are specifically designed for this application.[8]

Cationic phosphine ligands containing phenylguanidinium moieties were originally developed to make use of their pronounced solubility in water.[9,10] They have been shown to form active catalyst systems in Pd-mediated C–C coupling reactions between aryl iodides and alkynes[9,11] (Castro–Stephens–Sonogashira reaction) and Rh-catalysed hydroformylation of *n*-hexene in aqueous two-phase systems.[12]

In the present article, we report a new and very general approach to immobilise homogeneous Rh-catalysts in hexafluorophosphate ionic liquids. We found that the modification of neutral phophine ligands with cationic phenylguanidinium groups represents a very powerful tool to immobilise Rh complexes in these ionic liquids. In detail, we describe the synthesis of the new ligand **1a** and its catalytic performance in the biphasic, Rh-catalysed hydroformylation of oct-1-ene using the ionic liquid $[BMIM]PF_6$ as catalyst solvent. This ionic liquid has been prepared from [BMIM]Cl[13] according to a method described by Fuller and Carlin[14] or has been purchased from Solvent Innovation GmbH, Cologne.[15] First experiments aimed to prove the general concept by comparing the ligand PPh_3 with the related guanidinium-substituted ligand **2a** (Table 1, entries 1–5). **2a** was prepared from **2b** by anion exchange with NH_4PF_6 in aqueous solution. **2b** was prepared as previously described by Stelzer *et al.*[10]

In the reaction with PPh_3, good catalytic activity is observed but obviously a significant part of the hydroformylation reaction takes place in the organic layer. After the first catalytic run, 53% of the used Rh is found in the organic layer (according to ICP analysis) (Table 1, entry 1). In contrast, with ligand **2a** the hydroformylation reaction takes place uniquely in the ionic liquid layer (Table 1, entries 3, 4). In the first catalytic run the hydroformylation activity was found to be lower than in the case of PPh_3 (probably due to some mass transfer limitation of oct-1-ene into the ionic liquid). However, due to the excellent immobilisation of the Rh-catalyst with **2a** (leaching is < 0.07% per run according to ICP analysis (detection limit)), the catalytic activity of the ionic catalyst solution is even slightly higher in the third recycling run compared to the first run (probably due to some preformation time of the active catalyst). Since NaTPPTS is the most widely used ligand for immobilisation of Rh-catalysts in aqueous catalyst phases, this ligand was tested as well (Table 1, entries 5, 6). The results reveal good immobilisation of the Rh-complex in the ionic liquid but much lower activity of the resulting catalyst in the hydroformylation of oct-1-ene in comparison with **2a**.



1a: R = R', X = I
1b: R = phenyl
1c: R = H

2a: X = PF_6
2b: X = I

Encouraged by the good results with the guanidinium-substituted ligand, we decided to adopt this new immobilisation

Table 1 Hydroformylation results with different ligands in $[BMIM]PF_6$

No.	Ligand (cycle)	Conversion (%)	TOF[a] h^{-1}	Octane + i-octenes (%)	n : iso[b]
1	PPh_3 (1)	69.1	680	0.4	2.8
2	PPh_3 (3)	10.2	100	0.1	2.7
3	**2a** (1)	32.1	276	2.5	2.0
4	**2a** (3)	35.3	330	3.5	1.7
5	NaTPPTS	7.8	80	4.9	2.6
6	NaTPPTS	7.7	78	4.9	2.6
7	**1a** (1)	10.6	15	1.5	19.1
8	**1a** (3)	21.9	30	2.4	20.9
9	**1a** (5)	38.3	52	3.4	21.3
10	**1a** (7)	44.3	58	3.9	18.0

[a] Turnover frequency (TOF) in mol of octene converted per mol of Rh per h. [b] Ratio of linear to branched aldehyde products; general conditions: $CO:H_2$ = 1; $p(CO/H_2)$ = 30 bar; T = 100 °C; L : Rh = 2; Rh-precursor: $Rh(CO)_2acac$, preformation time 30 min; t = 1 h (runs 1–6), 8 h (runs 7–10).

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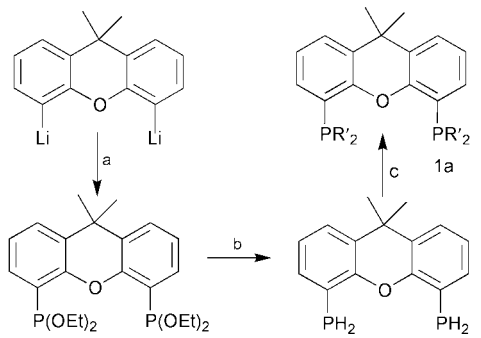
concept to a ligand structure that promises better regioselectivity in the hydroformylation reaction. It is well-known that diphosphine ligands with large natural P–metal–P bite angles form catalysts for highly regioselective hydroformylation reactions.[16] Here, xanthene-type ligands (P–metal–P ~110°) developed from van Leeuwen's group proved to be especially suitable showing, *e.g.* an overall selectivity of 98% towards the desired linear aldeyde in oct-1-ene hydroformylataion.[17–19] Recently, some work has been published where xanthene-based ligands have been immobilised on silica support.[20]

We describe here the first use of xanthene-based ligands in biphasic catalysis using ionic liquids as catalyst solvent. Since xanthene ligands such as, *e.g.* **1b** show highly preferential solubility in the organic phase in a biphasic oct-1-ene/[BMIM]PF_6 mixture, even at rt we developed the guanidinium-modified xanthene ligand **1a** for this purpose. The cationic ligand **1a** was synthesised in four steps according to Scheme 1.†



Scheme 1 Synthesis of ligand **1a**. a) diethylchlorophosphite; b) $LiAlH_4$–chlorotrimethylsilane; c) 4 eq. 3-iodophenylguanidine, 2 mol% Pd_2dba_3 * $CHCl_3$, 80 °C, 24 h in DMF.

The structure of **1a** was established by its mass spectrum and its $^{31}P\{^1H\}$NMR chemical shift ($\delta P = -15.9$) comparable to that of **1b** ($\delta P = -17.9$)[21] and of the *meta* guanidinium phosphines **2a** ($\delta P = -4.7$).[10] The signal at $\delta C = 157.1$ in the $^{13}C\{^1H\}$NMR spectrum of **1a** may be assigned to the carbonium carbon atoms of the guanidinium moieties, the δC value of which compares well with that in **2a**[10] ($\delta C = 155.8$). Some of the $^{13}C\{^1H\}$NMR resonances appear as higher order line pattern (X-parts of AA′X spin systems, A, A′ = ^{31}P, X = ^{13}C) in agreement with the diphosphine structure proposed for **1a**.

After each hydroformylation run, in which **1a** was used as crude product, the organic layer was decanted off (under normal atmosphere) and the remaining ionic catalyst layer remained in the autoclave for the next run. It is noteworthy that the catalytic activity increases during the first runs to obtain a stable level only after the forth recycling run (Table 1, entries 7–10). This behaviour is attributed to a certain catalyst preforming time as well as to impurities of 3-iodophenylguanidine in the used ligand sample (about 5 mass%). The latter are slowly washed out from the catalyst layer over the first catalytic runs. After ten consecutive runs an overall turnover number of 3500 mol oct-1-ene per mol Rh-catalyst could be obtained. In good agreement with the recycling experiments, the Rh-leaching into the organic layer was found to be very low. With AAS and ICP analysis no rhodium could be detected in the organic layer indicating a leaching of less than 0.07%. In all experiments with **1a** very good selectivities for the linear aldehyde were obtained thus proving that the attachment of the guanidinium moiety to the xanthene backbone does not influence its known positive effect on the regioselectivity of the reaction. This is in line with previous IR and NMR studies in our laboratories showing that the steric and electronic properties of arylphosphines is not significantly changed by introduction of polar groups like SO_3^-, PO_3^{2-} and guanidinium in *meta*- or *para*-position to phosphorus.[10]

In conclusion, we could show that the modification of known phosphine ligands with guanidinium groups represents a simple and very efficient method to fully immobilise transition metal complexes in hexafluorophosphate ionic liquids. Hereby, the electronic properties of the phosphine is not changed significantly. Our approach may therefore be of interest not only for hydroformylations but also for many other catalytic reactions in ionic liquids. Further work to develop methods for the immobilisation of neutral catalyst complexes in ionic liquids is in progress.

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Notes and references

† *Preparation of* **1a**: to a solution of 0.75 g (2.74 mmol) of the diprimary phosphine **1c** (prepared according to van Leeuwen *et al.*[22]) and 3.17 g (10.96 mmol) of 3-iodophenylguanidine 227 mg (2 mol%) of tris(benzylidene acetone)dipalladium(0) were added and the reaction mixture was heated to 80–100 °C for 24 h. $^{31}P\{^1H\}$ NMR spectroscopic control of the reaction mixture indicated that all of the diprimary phosphine had been consumed. On evaporation of the solvent *in vacuo* (80 °C, 0.01 mbar) 4.14 g of a yellow–brownish coloured powder were obtained. It contains small amounts of 3-iodophenylguanidine as indicated by the $^{13}C\{^1H\}$-NMR spectrum.

Mass spectrum [SIMS(DTE/DTT/Sul)]: cation: *m/z* = 919; $^{31}P\{^1H\}$-NMR data (161.98 MHz, 298 K, d_4-methanol, referenced to H_3PO_4) for **1a**: $\delta P = -15.9$. $^{13}C\{^1H\}$-NMR *data* (100.63 MHz, 298 K, d_4-methanol, referenced to TMS_{int}, values in parentheses $N = J_{PC} + J_{P'C}$) for **1a**: 157.1, 153.3 (*C*–O, 19.3 Hz), 141.0, 139.9 (13.2 Hz), 139.1 (6.0 Hz), 133.1 (12.0 Hz), 132.9, 131.5, 131.1 (6.0 Hz), 130.6 (19.3 Hz), 128.6, 126.2, 125.2, 39.5 (N*Me*$_2$), 35.5 (*C*Me$_2$), 32.3 (C*Me*$_2$).

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