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Ionic liquids in regioselective platinum-catalysed hydroformylation

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Dedicated to Prof. Dr. Wilhelm Keim on the occasion of his 65th birthday

Abstract

The regioselective, platinum-catalysed hydroformylation of functionalized and non-functionalized olefins was chosen to demonstrate the great potential of room temperature liquid chlorostannate ionic liquids as solvents for homogeneous catalysis. The moderate Lewis-acidity of these ionic liquids allows the activation of the Pt-catalyst combined with tolerance of the functional groups in the substrate. Dissolved in chlorostannate ionic liquids, the Pt-catalyst shows enhanced stability and selectivity in the hydroformylation of methyl-3-pentenoate (M3P) compared to the identical reaction in conventional organic solvents. In the case of 1-octene hydroformylation, a biphasic reaction system could be realised using the chlorostannate ionic liquids as catalyst solvents. Besides the catalytic results, a method to determine the Lewis-acidity of chlorostannate ionic liquids by ^{119}Sn NMR is presented.

Keywords: Ionic liquids; Chlorostannate melt; Hydroformylation; Methyl-3-pentenoate; Biphasic catalysis

1. Introduction

A new approach has been introduced to catalyst separation and recycling in homogeneous catalysis involving the use of solvents known as ionic liquids. Ionic liquids are salts that melt at ambient temperature (<100°C) [1–3].

The first application of room temperature ionic liquids in hydroformylation was reported by Chauvin et al. [4,5]. They describe the biphasic hydroformylation of 1-pentene with [$Rh(CO)_2$acac] in 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM PF_6). The biphasic mode of the reaction mixture allowed principally a catalyst recovery by simple phase separation.

We became interested in using ionic liquids for the hydroformylation of functionalized olefins. In the Rh-catalysed hydroformylation of methyl-3-pentenoate (M3P), we could show that the addition of an ionic liquid increases significantly the catalyst's lifetime and overall productivity [6]. The latter is achieved by a distillation process under reaction conditions. The catalyst is stabilised by the non-volatile ionic liquid under the conditions of distillation. The catalyst can be reused several times without additional regeneration and without significant loss in activity and selectivity. These encouraging results stimulated further work in our group aiming at other hydroformylation reactions in ionic liquids.

Besides the industrially used Rh- and Co-catalysts, platinum(II) complexes with phosphine ligands pro-

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moted by $SnCl_2$ are known as hydroformylation catalysts since 1976 [7]. Systems with monodentate phosphines have been investigated in the hydroformylation of terminal and internal olefins [8–15]. Pt/Sn-catalysts with diphosphines have been successfully applied to the asymmetric hydroformylation [16–20] and to the highly regioselective hydroformylation of internal, functionalized olefins [21].

The platinum-catalysed hydroformylation of ethylene in a tetraethylammoniumchlorostannate molten salt (melting point: 78°C) was described by Parshall [22] as early as 1972. This publication showed for the first time the potential of a chlorostannate ionic liquid as reaction medium for a homogeneous platinum-catalyst. However, the relatively high melting point of the chlorostannate salt used by Parshall caused some restrictions for reaction parameters and processing conditions. The experiments were carried out under extreme conditions (syngas pressure of 400 bar). Finally, in Parshall's publication, the activity of the catalyst has not been determined quantitatively. Therefore, it is not possible to compare the obtained data with results in conventional organic solvents.

In order to explore in more detail the catalytic potential of Pt-complexes in chlorostannate melts, we investigated the regioselective hydroformylation of functionalized and non-functionalized alkenes in room temperature liquid chlorostannate ionic liquids. Those low melting chlorostannate salts have been recently described by Ling and Koura [23] as solvents for electrodeposition of tin and other electrochemical applications.

In our contribution, we describe for the first time the use of a room temperature liquid chlorostannate ionic liquid as reaction medium for a homogeneous catalyst. In detail, the hydroformylation of 1-octene and methyl-3-pentenoate (M3P) with $(PPh_3)_2PtCl_2$ in slightly Lewis-acidic chlorostannate ionic liquids is reported.

2. Experimental

2.1. Reagents

All reactions were performed under argon using standard Schlenk tube techniques. Solids were dried under reduced pressure and liquids were distilled over appropriate desiccating agents prior to use [24]. 1-Butyl-3-methylimidazoliumchloride (BMIM Cl **1**) (Elementis Specialitis), $SnCl_2$ (Sigma–Aldrich), PPh_3 (Sigma–Aldrich) and $PtCl_2$ (Degussa-Hüls) were used without further purification. ^{119}Sn NMR spectra were recorded with a Bruker AC 300-spectrometer.

$$[\text{cation}]^+ Cl^- + SnCl_2 \rightleftharpoons [\text{cation}]^+ SnCl_3^-$$

$$[\text{cation}]^+ SnCl_3^- + SnCl_2 \rightleftharpoons [\text{cation}]^+ Sn_2Cl_5^-$$

Scheme 1. Ionic liquids based on trichlorostannate anions.

2.2. Preparation of slightly acidic chlorostannate ionic liquids

Slightly Lewis-acidic chlorostannate ionic liquids were synthesised by mixing **1** or 1-butyl-4-methylpyridinium chloride (4-MBP Cl) **2** with $SnCl_2$ in a molar ratio of 1:1.04 [49 mol% chloride salt/51 mol% $SnCl_2$; $X(SnCl_2)=0.51$]. **2** was prepared by reacting 1 equivalent of 4-methylpyridine with 1.5 equivalents of butylchloride under reflux conditions for 120 h. The product formed a white, sometimes slightly rose solid which was filtered off and dried.

The ionic liquids were obtained by formation of the anions $SnCl_3^-$ and $Sn_2Cl_5^-$ as shown in Scheme 1 [23]. Both chlorostannate melts are slightly yellow liquids at room temperature (melting points <25°C).

Generally, the Lewis-acidity of a chlorostannate ionic liquid is determined by its chloride salt/$SnCl_2$ ratio. To characterise our chlorostannate ionic liquids, we developed a method to determine its Lewis-acidity by ^{119}Sn NMR spectroscopy. Fig. 1 shows the correlation between the acidity of **1**/$SnCl_2$ and the chemical shift of its ^{119}Sn NMR signal. Using this calibration curve, the Lewis-acidity of an ionic liquid of unknown composition can be easily determined. The observation that only one ^{119}Sn NMR signal is detected for all chloride salt/$SnCl_2$ compositions is related to a fast exchange between $[SnCl_3]^-$ and $[Sn_2Cl_5]^-$ in the melt at room temperature.

To form the ionic catalyst solution, $(PPh_3)_2PtCl_2$ (synthesised according to Ref. [25]) was added to the chlorostannate ionic liquids. A change in colour from yellow to red was observed. Probably, this is attributed to the abstraction of chloride atoms from the platinum-complex by the acidic $Sn_2Cl_5^-$ of the

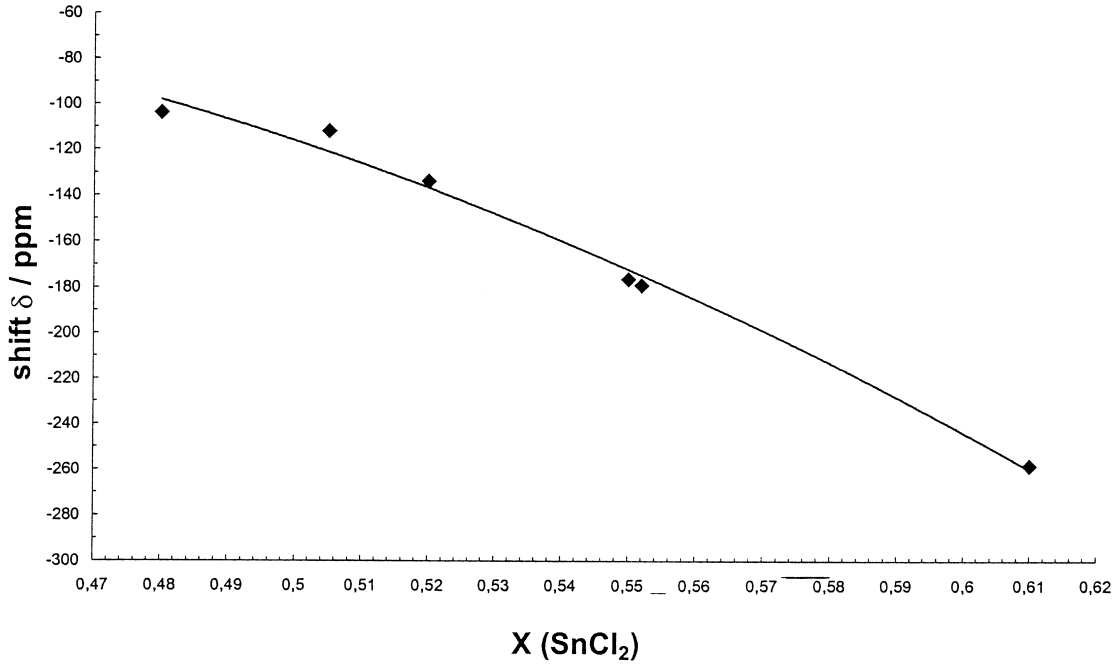


Fig. 1. **1**/$SnCl_2$: Correlation between the Lewis-acidity of the chlorostannate ionic liquid and its ^{119}Sn NMR shift [X($SnCl_2$)=mol $SnCl_2$/(mol $SnCl_2$+mol **1**)].

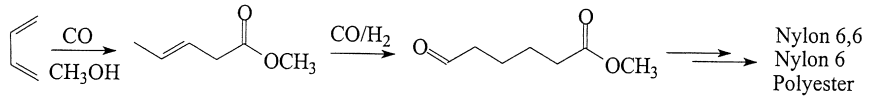
ionic liquid. This assumption could be supported by recording the Lewis-acidity of the chlorostannate ionic liquid before and after the addition of $(PPh_3)_2PtCl_2$ by ^{119}Sn NMR. The acidity of the ionic liquid was found to be significantly reduced after the addition of the Pt-complex. Moreover, the amount of this reduction corresponded very well to the assumption of an acid–base reaction of both chloride atoms from the platinum-complex with the acidic ionic liquid. Obviously, this acid–base reaction plays an important role for the formation of the catalytic active Pt-complex in the chlorostannate ionic liquid.

2.3. Hydroformylation experiments in CH_2Cl_2

In a typical experiment, 0.02 mmol of $(PPh_3)_2PtCl_2$ and 0.1 mmol of $SnCl_2$ were dissolved in 10 ml dichloromethane and stirred for 30 min. The solution was transferred into a previously dried 75-ml stainless steel autoclave under argon. The vessel was pressurised with syngas (1:1) to reaction pressure, placed in a preheated oil bath, and stirred with a magnetic stirrer. After 30 min preforming time, the pressure was reduced to the reaction pressure and the olefin was added through a dropping funnel. After reaction time, the autoclave was cooled in an ice bath to room temperature. After venting the autoclave, the yellow solution was analysed by GC with di-*n*-butylether as internal standard. The products were characterised by GC-MS, GC-IR and NMR-spectroscopy.

2.4. Hydroformylation experiments in chlorostannate ionic liquids

In a typical experiment, 0.02 mmol of $(PPh_3)_2PtCl_2$ were dissolved in 10 ml of the chlorostannate ionic liquid [X($SnCl_2$)=0.51] and stirred for 30 min. The solution was transferred into a previously dried 75-ml stainless steel autoclave under argon. The vessel was pressurised with syngas (1:1) to the reaction pressure, placed in a preheated oil bath, and stirred with a magnetic stirrer. After 30 min preforming time, the pressure was reduced to the reaction pressure and the olefin was added through a dropping funnel. After reaction time, the autoclave was cooled in an ice bath to room temperature. In case of the monophasic



Scheme 2. Alternative route to produce adipinic acid from butadiene.

hydroformylation of M3P, the organic compounds were separated from the ionic catalyst layer by flash distillation at reaction temperature and high vacuum. In case of the biphasic hydroformylation of 1-octene, the organic compounds were isolated by a simple phase separation.

The colourless organic solution was analysed by GC with di-*n*-butylether as internal standard. The products were characterised by GC-MS, GC-IR and NMR-spectroscopy.

3. Catalytic results and discussion

3.1. Hydroformylation of M3P

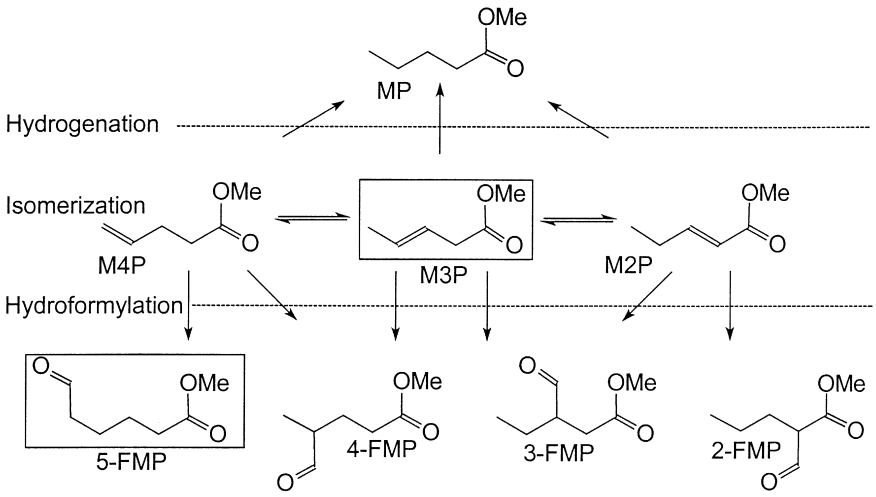
The regioselective hydroformylation of M3P offers an alternative route to produce adipinic acid from butadiene (see Scheme 2).

To obtain 5-formylmethylpentenoate (5-FMP), it is necessary to combine an isomerisation step with a highly regioselective hydroformylation. Scheme 3 shows the different reaction pathways in the hydroformylation of M3P.

It is noteworthy that M3P is fully mixable with CH_2Cl_2 as well as with the chlorostannate ionic liquids used in our experiments (**1**/$SnCl_2$ and **2**/$SnCl_2$). CH_2Cl_2 was chosen as organic solvent for the comparison experiments due to the fact that it was found to be the best organic solvent for hydroformylation reactions with the Pt/Sn-catalyst system [22].

As shown in Table 1, the overall activity of the platinum-catalyst is significantly higher in the chlorostannate ionic liquids in comparison to CH_2Cl_2 (comparison of entries a, b with c). This result is probably caused by an enhancement of catalyst lifetime in the ionic liquid solvent. In CH_2Cl_2, the Pt-catalyst is completely deactivated during the reaction even if a fivefold excess of ligand is used to stabilise the catalyst. Under identical conditions, the catalyst still shows some activity after the reaction time in chlorostannate ionic liquids.

In all three experiments, only hydroformylation and hydrogenation products were detected in significant



Scheme 3. Reaction pathways in the hydroformylation of M3P.

Table 1
Comparison of different solvents in the hydroformylation of methyl-3-pentenoate (M3P)

Entry	Solvent	Conversion [%]	TOF[a] [h^{-1}]	S(5-FMP)[b] [%]	S(MP)[c] [%]
a	**2**/$SnCl_2$	5.4	31	56.5	9.6
b	**1**/$SnCl_2$	6.3	37	56.5	9.8
c	CH_2Cl_2	1.5	9	44.4	4.6

Conditions: 0.02 mmol $PtCl_2(PPh_3)_2$, 0.1 mmol PPh_3, 20 mmol M3P, 5 ml solvent, $p(CO/H_2)$=50 bar, T=120°C, t=2 h, Entries a, b: X($SnCl_2$)=0.51.

[a]Turnover frequency (TOF)= mol of M3P converted per mol of Pt-catalyst per hour.

[b]The selectivity for 5-FMP was calculated in the following way: [S(5-FMP)]=amount of 5-FMP/amount of all hydroformylation products.

[c]The selectivity for methylpentanoate (MP) was calculated in the following way: [S(MP)]=amount of MP/amount of all products.

Table 2
Comparison of different solvents in the hydroformylation of 1-octene

Entry	Solvent	Conversion [%]	TOF[a] [h^{-1}]	S(*n*-nonanal)[b] [%]	S(octane)[c] [%]
a	**2**/$SnCl_2$	19.7	103	96.0	29.4
b	**1**/$SnCl_2$	22.3	126	95.0	41.7
c	CH_2Cl_2	25.7	140	98.3	9.4

Conditions: 0.02 mmol $PtCl_2(PPh_3)_2$, 0.1 mmol PPh_3, 20 mmol 1-octene, 5 ml solvent, $p(CO/H_2)$=90 bar, T=120°C, t=2 h, , Entries a, b: X($SnCl_2$)=0.51.

[a]Turnover frequency (TOF)= mol of 1-octene converted per mol of Pt-catalyst per hour.

[b]The selectivity for *n*-nonanal was calculated in the following way: [S(*n*-nonanal)]=amount of *n*-nonanal/amount of all hydroformylation products.

[c]The selectivity for octane was calculated in the following way: [S(octane)]=amount of octane/amount of all products.

amounts. The higher hydrogenation activity of the ionic system may be attributed to a selective gas solubility of the ionic medium. Under reaction conditions, the hydrogen of the syngas seems to have a higher solubility in the chlorostannate ionic liquid than CO. This may be the reason for the higher hydrogenation activity observed for the ionic liquid system. For further confirmation of this assumption, catalytic experiments with lower H_2/CO-ratio in the syngas have been carried out. However, the overall catalytic activity was much lower in these cases. Therefore, it was not possible to prove the expected solubility influence on the catalytic hydrogenation activity.

3.2. Hydroformylation of 1-octene

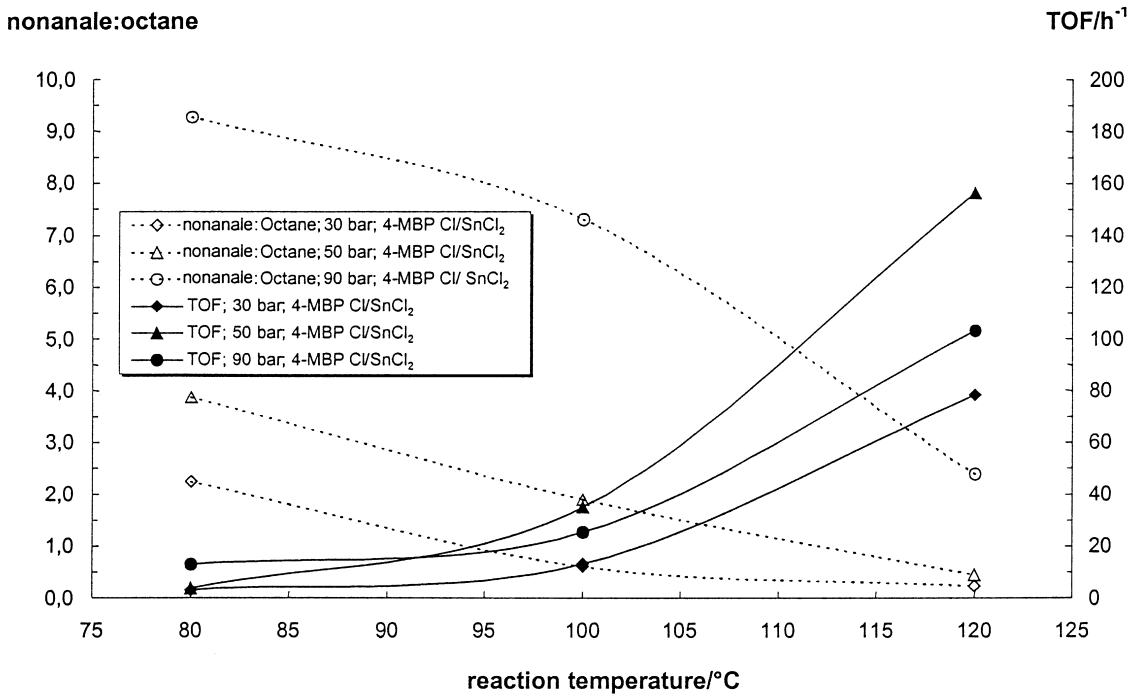
The hydroformylation of 1-octene, which is of interest for the synthesis of linear nonanal, was chosen as second model reaction for the use of $(PPh_3)_2PtCl_2$ in chlorostannate ionic liquids. To produce the technically desired *n*-nonanal in high selectivity, it is necessary to achieve a highly regioselective hydroformylation. While the hydroformylation of small olefins ($<C_5$) is technically realised in a biphasic aqueous system, this method suffers from low reaction rates for the 1-octene hydroformylation due to low olefin solubility in water.

Table 2 shows the results obtained with $(PPh_3)_2PtCl_2$ in two different chlorostannate ionic liquids in comparison to the experiment in CH_2Cl_2 under identical conditions. While the reaction is monophasic in CH_2Cl_2, a biphasic reaction takes place with each of the chlorostannate ionic liquids. Moreover, no leaching of the Pt-catalyst was detected, which can be interpreted as another strong hint for the postulated ionic structure of the active Pt-catalyst. The ionic catalyst solution can be recovered after catalysis by simple phase separation.

The hydroformylation of 1-octene with $(PPh_3)_2PtCl_2$ in CH_2Cl_2 shows (in good accordance to Ref. [22]) reasonable activity with very high selectivity to the linear nonanal (entry c in Table 2). The undesired hydrogenation of 1-octene to octane is moderate in CH_2Cl_2. In contrast, the results in both chlorostannate ionic liquids show slightly lower rate, still very high *n*/*iso*-selectivity, but higher hydrogenation activity (entries a and b in Table 2). The latter effect was already found for the hydroformylation of M3P. Interestingly, in this case, the undesired hydrogenation activity depends significantly on the cation of the ionic liquid (41.7% hydrogenated product with BMIM vs. 29.4% with 4-MBP).

The promising results in the biphasic system with **2**/$SnCl_2$ prompted further studies to investigate the influence of temperature and syngas pressure on the hydroformylation and hydrogenation activity of the Pt-catalyst in the ionic liquid. The results obtained are summarised in Scheme 4.

The highest ratio of hydroformylation to hydrogenation is found at high syngas pressure and low temper-



Scheme 4. Temperature and pressure dependence of the hydroformylation of 1-octene with $PtCl_2(PPh_3)_2$ in **2**/$SnCl_2$.

ature. At 80°C and 90 bar CO/H_2-pressure more than 90% of all products are *n*-nonanal and *iso*-nonanal, the ratio between these two hydroformylation products being 98.6:1.4 (*n*:*i*=72.4). Generally, very high selectivities for the linear aldeyd (always >95%) are found in all experiments presented in Scheme 4. At high temperatures, the overall activity increases in all experiments. However, this is very much related to an increasing hydrogenation activity of the system. In contrast, higher syngas pressure favours the hydroformylation reaction over the hydrogenation of the feedstock. This result is probably caused by the fact that only at high syngas pressure does the ionic liquid dissolve enough CO to allow competitive hydroformylation reactivity of the Pt-complex.

4. Conclusion

Our results show that room temperature liquid chlorostannate ionic liquids are versatile solvents for homogeneous catalysts such as $(PPh_3)_2PtCl_2$. The Pt-complex dissolved in a slightly acidic chlorostannate ionic liquids is an active catalyst for the regioselective hydroformylation of methyl-3-pentenoate and 1-octene. Moreover, our results of the regioselective hydroformylation of methyl-3-pentenoate reveal some unique properties of the chlorostannate ionic liquid. In contrast to other known ionic liquids, the chlorostannate system combine a certain Lewis-acidity with high compatibility for functional groups. The first led in our experiments to the activation of $(PPh_3)_2PtCl_2$ by a Lewis-acid–base reaction with the acidic ionic liquid medium. The high compatibility for functional groups could be demonstrated by the catalytic reaction with methyl-3-pentenoate. Generally, we think that the unique Lewis-acidic properties of such chlorostannate ionic liquids could prove to be useful for a wide range of other catalytic and synthetic applications.

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