# COMMUNICATIONS

# Triphasic Liquid Systems for Improved Separations. Trioctylmethylammonium Chloride-Immobilised Rhodium Trichloride: A Phosphine-Free Hydroformylation Catalytic System

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**Abstract:** A liquid triphasic system made of isooctane, water, and trioctylmethylammonium chloride allows one to carry out the hydroformylation of model olefins using neat $RhCl_3$ as catalyst precursor. By using the triphasic system, the catalyst is kept separate from the reagents and products. This allows one to simply remove the product and to recycle the catalyst numerous times. No leaching of rhodium into the organic phase is observed.

**Keywords:** hydroformylation; ionic liquids; multiphase catalysis; rhodium; water

Hydroformylation is one of the largest volume processes in the chemical industry that uses homogeneous metal catalysis. Efficient catalyst separation remains, however, one of the key issues for the clean isolation of products and for catalyst recycling. The archetype example of the sought-after separation of the catalytic system is still the Ruhrchemie/Rhône–Poulenc process for the aqueous hydroformylation of propene. In this case the Rh catalyst is made water-soluble and can be easily separated from the reaction products.[1]

The techniques used to keep hydroformylation products and catalysts apart often involve partitioning of the two between immiscible liquid phases.[2] Final separation is then obtained by decanting. For example, methylated cylodextrins can be employed in the hydroformylation of olefins in an aqueous-organic system.[3] Other examples include catalysis using biphasic fluorous solvent systems,[4] and the use of supercritical fluids.[5] Ionic liquids have attracted attention in this field as well, due to their combined ability to form biphasic systems with organic species, and to retain catalytic metal complexes.[6]

More recently, hydroformylation techniques based on the heterogenisation of the catalytic species using

supported ionic liquid catalysis (SILP) have also been described,[7] along the lines of the supported aqueous phase catalysis (SAPC) developed earlier by Davis.[8] Leitner and co-workers have instead addressed the separation issue through the design of a $CO_2$-regulated reaction/separation systems where the substitution at the metal catalyst makes it soluble during the hydroformylation reaction, and insoluble in the separation stage.[9] All the above cases are inventive and efficient, but the presence of a phosphine ligand as catalyst activator is always necessary, and labourious synthetic steps are often required.

A different class of promising multiphasic systems is that made by more than two mutually insoluble liquid phases (e.g., organic/aqueous/ionic). These represent a valuable tool for *in situ* separation of products, by-products, and catalysts; and for the simple recovery and recycle of the latter. In addition, often the catalyst efficiency can be boosted by choosing the appropriate ionic liquid phase to immobilise the catalyst. A number of such multiphasic systems has been reviewed recently, homogeneous,[2] as well as heterogeneous.[10]

Our experience dates back to the use of liquid onium salt-modified heterogeneous catalysts.[11] More recently, we have described a triphasic system made of trioctylmethylammonium chloride/isooctane/water that promoted the formation, immobilisation, and stabilisation of recyclable palladium nanoparticles starting from appropriate Pd complexes. These were catalytically active for selective hydrodehalogenation and Heck coupling reactions, and allowed easy product-catalyst separation thanks to triphasic separation, as well as straightforward catalyst recycle.[12] A biphasic system for catalytic hydroformylation was also reported, based on the use of water-soluble protein-rhodium complexes.[13] In this instance, the catalytic system allowed facile recovery of the Rh-HSA (human serum albumin) complex with high chemo- and regioselectivity in the hydroformylation reaction.

In the present paper, we turn our attention to hydroformylation in a triphasic organic/aqueous/ionic

system where the catalyst is neat $RhCl_3$ immobilised in a trioctylmethylammonium chloride $[(C_8H_{17})_3N^+CH_3Cl^- = TOMAC]$ phase. The driving force of this study is the improved separation and recycle of the catalyst, as well as simplification of the standard operating procedures, thanks (i) to the use of one of the most widely available Rh precursors "as such", that is, without any activation or synthetic step, and (ii) thanks to the lack of any additional catalyst ligand/activator, such as phosphines. Rhodium trichloride as a hydroformylation catalyst has, in fact, been described, mostly however in conjunction with an activator, for example, alkyl- or arylphosphines or nitrogen-containing ligands.[14]

RhCl$_3$ was reported as a hydrogenation and isomerisation catalyst under phase-transfer catalysis conditions in a biphasic aqueous-organic system, in the presence of Aliquat 336 (a commercial mixture consisting predominantly of TOMAC $[(C_8H_{17})_3N^+CH_3Cl^-]$).[15,16] In this case the suggested soluble catalyst precursor was the ion pair $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$, based on an elemental analysis of the related species $[(C_7H_{15})_4N]^+$ $[RhCl_3Br]^-$, and on the correlation between the concentration of Aliquat 336 and the partition coefficient of the metal ion between the organic and aqueous phases [Eq. (1)].[16]

$$Q^+Cl^-_{(org)} + RhCl_{3(aq)} \rightleftharpoons Q^+RhCl_4^-_{(org)} \qquad (1)$$

$$Q^+ = (C_8H_{17})_3N^+CH_3$$
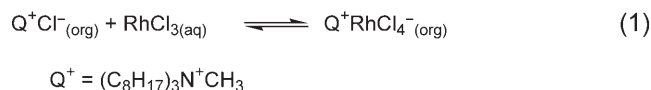
The difficulty in this case was in the incomplete recovery of the catalyst, that had to be re-extracted repeatedly from the organic to the aqueous phase by ion exchange with sodium perchlorate.

Exploratory tests on the triphasic hydroformylation catalytic system were run on the model reaction of styrene with syngas [Eq. (2)] by using 10 mol%



$$(2)$$
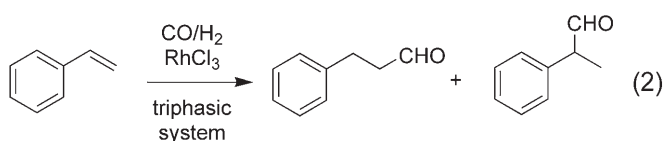
RhCl$_3$ as the catalyst and 1.0 mL of TOMAC , the results are shown in Table 1.

The initial experiment was conducted using a biphasic TOMAC/isooctane system, on the lines of reported procedures where the catalyst is kept separate from reagents and products by the use of an ionic liquid phase.[17] The RhCl$_3$ catalyst was dissolved in TOMAC, the reagent in isooctane, and the biphasic mixture was reacted under 90 atm of syngas at 80°C (run 1). No reaction occurred.

**Table 1.** Hydroformylation of styrene catalysed by RhCl$_3$ in water/TOMAC/isooctane triphasic system.[a]

| Run | $T$ [°C] | $t$ [h] | Conv. [%] | Aldehyde yield [%] | Branched/linear [%] |
|-----|------|------|------|------|------|
| 1[b] | 80 | 18 | - | - | - |
| 2 | | 16 | 100 | 100 | 98/2 |
| 3[c] | | 16 | 100 | 100 | 99/1 |
| 4[c] | | 16 | 100 | 100 | 98/2 |
| 5[c] | | 16 | 100 | 100 | 98/2 |
| 6[d] | | 16 | 1 | 1 | 100 |
| 7[c,e] | | 18 | 100 | 100 | 96/4 |
| 8 | 60 | 18 | 57 | 57 | >99 |
| 9[c] | | 18 | 55 | 55 | >99 |
| 10[c] | | 18 | 54 | 54 | >99 |
| 11[f] | 80 | 5 | 99 | 99 | 98/2 |

[a] Substrate = 1.0 mmol; RhCl$_3$ = 0.10 mmol; isooctane/H$_2$O/TOMAC = 4/4/1 mL; $p(CO) = p(H_2) = 45$ atm. TOMAC = trioctylmethylammonium chloride.

[b] Experiment carried out without water. At the end of the reaction the organic isooctane phase is colourless and RhCl$_3$ is completely dissolved in TOMAC.

[c] Reaction carried out by using the catalytic phase recovered from the previous experiment.

[d] Reaction carried out by using a styrene to rhodium molar ratio = 100/1.

[e] To the TOMAC with dissolved RhCl$_3$ recovered from experiment 1, was added water (4 mL), isooctane (4 mL) and styrene (1 mmol).

[f] Experiment catalysed by RhCl$_3$ dissolved in water (4 mL) with isooctane (without TOMAC): at the end of the reaction rhodium leaching is complete.

On the other hand, the same reaction conducted in the presence of a third phase made by water, yielded quantitative conversion of the aldehydes after 16 h, with 98% of the branched isomer (run 2), the same efficient reaction was observed by adding water to the residual mixture of run 1 and subjecting it to the same hydroformylation conditions (run 7). In all these cases the catalyst precursor remained dissolved exclusively in the TOMAC phase – presumably in the form $[(C_8H_{17})_3NCH_3]^+[RhCl_4]^-$ – and the TOMAC/Rh/water ensemble could be recycled 3 times with no detectable loss of activity (runs 3–5). A ten-fold reduction of the amount of RhCl$_3$ resulted in the reaction being practically inhibited (run 6). Lower temperatures resulted in slower reactions (run 8), albeit with equally reproducible recycling (runs 9 and 10). In the presence of a biphasic isooctane/water system, without TOMAC, the RhCl$_3$-catalysed hydroformylation of styrene was fast, but total leaching of rhodium species to the organic phase was observed, making separation and recycle impossible (run 11).

Therefore, the triphasic system effectively promoted the reaction, not only by allowing recovery and recycle of the catalytic system, but also by avoiding rho-

dium leaching (see later), and by a favourable effect due to the presence of water.

Water, in fact, was indispensable for the reaction to proceed, a fact that has been already observed in other instances of catalysts that are active in the presence of an ionic environment. For example, Davis's studies on supported aqueous-phase (SAP) hydroformylation using a sulphonated Rh catalyst, indicated that the water amount greatly influenced catalytic performance: a too low or too high water content was detrimental, the optimum amount being intermediate (4–12 wt%).[18] At low water loadings the Rh catalyst was strongly adsorbed to the surface of the support, it was very stable, but lost the mobility necessary for it to be active. At high water content (>20 wt%) the SAP materials lost activity and stability, approaching the behaviour of unsupported catalysts. The positive effect of water was also reported by Jeffery during his studies on the Pd-catalysed Heck reaction in the presence of tetraalkylammonium salts in water-organic systems. In that case the effect of water was explained by an extraction mechanism whereby the onium salt regenerates the active Pd(0) species in the organic phase by a phase-transfer mechanism.[19]

When the long-chain aliphatic olefin tetradecene was hydroformylated [Eq. (3)] in the triphasic system under the conditions of Table 1, practically complete conversion was observed after 21 h, and the TOMAC/Rh/water system was recycled for 5 times with identical results (solid bars Figure 1). No selectivity was observed: 1- and 2-formyl-tetradecane were observed in approximately equimolar amounts (cross-hatched and diagonal hatched bars, Figure 1), and up to 16% of products deriving from double bond isomerisation followed by hydroformylation were detected (hatched bars, Figure 1).

In this case the filtered clear organic phase was checked for leaching of rhodium by adding a different olefin – styrene (1 mmol) – 100 atm of syngas and heating to 80 °C for 24 h. Complete lack of conversion indicated no metal leaching into the organic phase.

Norbornene was also hydroformylated quantitatively in the triphasic system under the conditions of Table 1, with 91% selectivity towards the *exo* isomer [Eq. (4)]. Recycle of the catalytic system was again achieved simply, without any loss of activity. As a matter of fact conversion after the second run increased up to quantitative, likely due to the complete transformation of the rhodium trichloride into the active catalytic species (Figure 2).
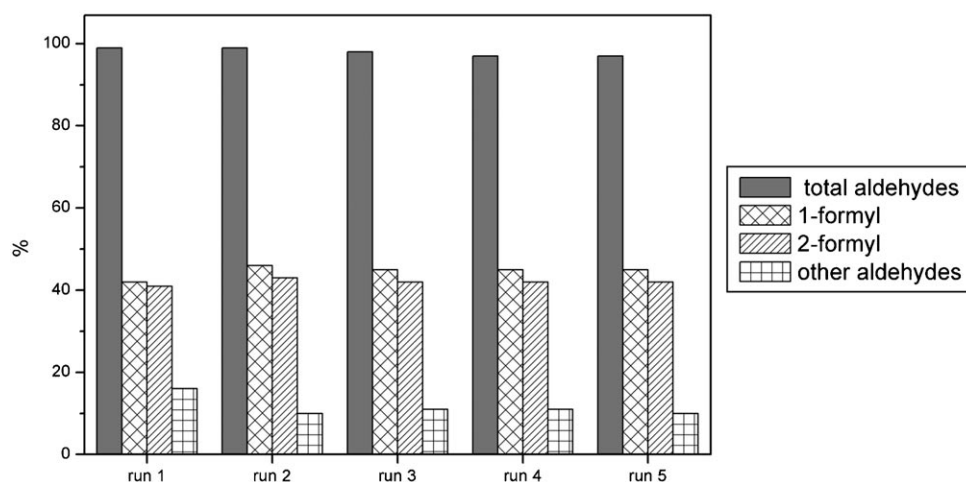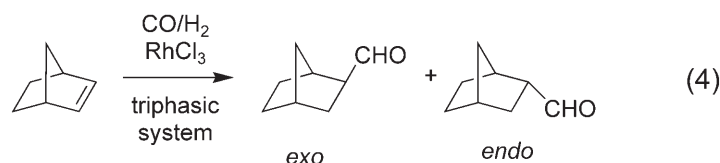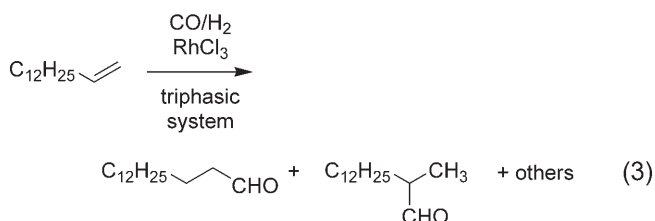
$$C_{12}H_{25}\diagup\diagup \xrightarrow[\text{triphasic system}]{\substack{\text{CO/H}_2 \\ \text{RhCl}_3}} C_{12}H_{25}\diagdown\diagup_{\text{CHO}} + C_{12}H_{25}\diagdown\underset{\text{CHO}}{\overset{\text{CH}_3}{\diagup}} + \text{others} \qquad (3)$$

$$\xrightarrow[\text{triphasic system}]{\substack{\text{CO/H}_2 \\ \text{RhCl}_3}} \quad \underset{exo}{\text{CHO}} \quad + \quad \underset{endo}{\text{CHO}} \qquad (4)$$



**Figure 1.** Hydroformylation of tetradecene (1 mmol), RhCl$_3$ (0.1 mmol), isooctane/H$_2$O/TOMAC=4/4/1 mL; $p$(CO)= $p$(H$_2$)=45 atm.

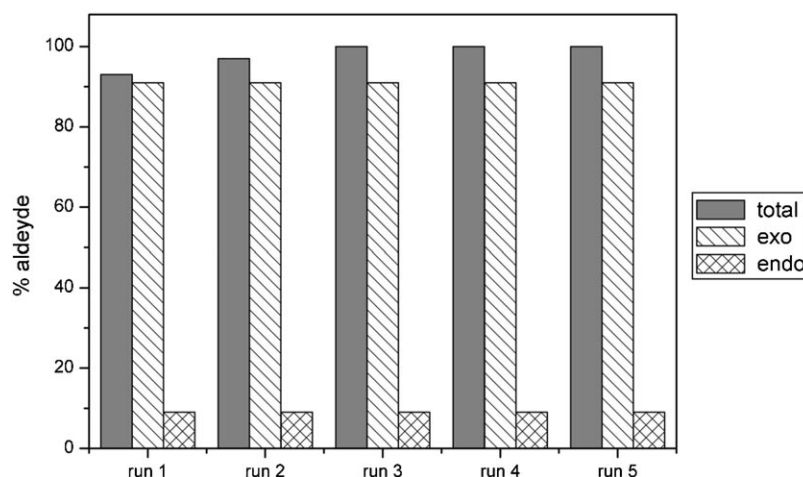**Figure 2.** Hydroformylation of norbornene (1 mmol), $RhCl_3$ (0.1 mmol), isooctane/$H_2O$/TOMAC$=4/4/1$ mL; $p(CO)=p(H_2)=45$ atm, $t=16$ h.

The active Rh species was not fully characterised due to the impossibility of extracting it from the ionic liquid phase without modifying its structure. However, the IR spectrum of the Rh-containing ionic liquid phase showed two sharp bands at 2063.7 and 1988.5 $cm^{-1}$, assigned to a rhodium carbonyl species (Figure 3).[20]

In conclusion, the triphasic system here described is active for the hydroformylation reaction of model olefins, and it allows simple recovery and recycle of the catalytic system for repeated runs, without detectable loss of activity, and without the need for phosphine ligands. In addition, the described triphasic system effectively prevents leaching of rhodium to the organic phase. This is of fundamental importance to avoid metal contamination of the products. The described hydroformylation is generally very efficient (yields

$>90\%$ at 80 °C), and regioselective: $>98\%$ branched aldehyde in the case of styrene, and $>90\%$ *exo* isomer in the case of norbornene.

Based on one other report, $RhCl_3$ likely forms an ion pair with TOMAC [Eq. (1)], this ion pair may represent the catalytic precursor which, under the reaction conditions, forms the catalytically active Rh-carbonyl species observed by IR. The formation of the ion pair might also explain the relatively high concentration of Rh (10 % mol) needed in this study. The large excess of TOMAC used here might mask the active catalyst when this is too diluted.

Noticeably, the presence of the aqueous phase is necessary for the reaction, a fact that is not clearly understood yet, but that might be connected either to increased mobility afforded by water within the TOMAC phase to the species involved in the reaction, or by a phase-transfer mechanism.
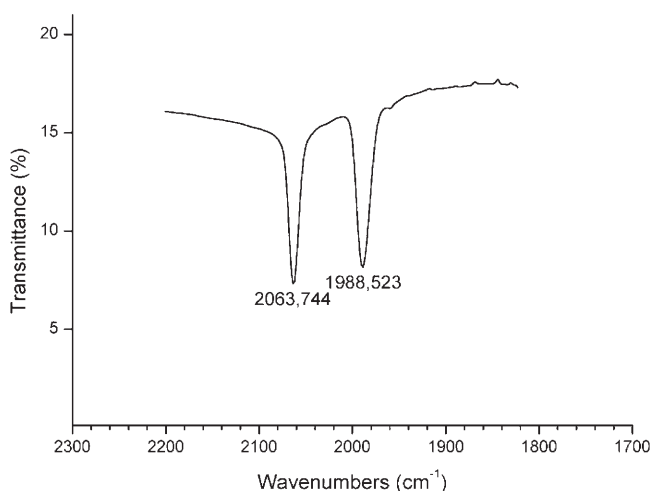


**Figure 3.** IR spectrum in the 2200–1800 $cm^{-1}$ region of the Rh-containing ionic liquid phase.

## Experimental Section

### Synthesis of Methyltri-*n*-octlyammonium Chloride (TOMAC)[21]

A 250 mL, round-bottomed flask equipped with a magnetic stirring bar was charged with 35.6 g (0.101 mol) of tri-*n*-octylamine and 40 mL of toluene. The mixture was placed under a nitrogen atmosphere and 13.0 g (0.106 mol) of dimethyl sulphate were added at room temperature. The mixture was heated in an oil bath kept at 140 °C for 18 h, then 2 mL of water were added and stirring was continued at 90 °C for additional 8 h. The mixture was cooled to room temperature and concentrated HCl (30 mL) was added. Following stirring of the biphasic mixture for 16 h, the aqueous phase was separated, and volatile material was removed under vacuum to afford methyltri-*n*-octylammonium chloride; yield: 42.5 g (99 %). $^1$H NMR (300 MHz, CDCl$_3$): δ=

0.81 (t, 9H, $J = 6.6$ Hz), 1.20–1.35 (m, 30H), 1.60 (br, 6H), 3.20 (s, 3H), 3.30 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 14.0, 22.3, 22.5, 26.3, 28.9, 29.0, 31.6, 52.2, 61.2.

## Triphasic Hydroformylation Catalysed by RhCl$_3$

To a glass tube containing TOMAC (1.0 mL) and H$_2$O (4.0 mL), RhCl$_3$ (0.1 mmol) was added and stirred until complete dissolution in the TOMAC phase. A solution of olefin (1.0 mmol) in isooctane (4.0 mL) was then added to the aqueous/ionic system. The tube was placed into a 150 mL stainless steel autoclave under nitrogen, pressurised to 90 atm with syngas (CO/H$_2$ = 1) and heated at 60–80 °C for the due time (see Table and plots). The reactor was then cooled to room temperature and the residual gases vented. The organic phase was separated, dried on Na$_2$SO$_4$ and the reaction products characterised by GC-MS.

## Acknowledgements

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