Unexpected Non-influence of the Phosphine/Rhodium Ratio on the Activity and Selectivity of Rhodium–Phosphine Hydroformylation Catalysts

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The activity and regioselectivity of rhodium hydroformylation catalysts containing 1,2,5-triphenylphosphole as ligand are independent of the Rh/1,2,5-triphenylphosphole ratio in the catalytic hydroformylation of alkenes.

Hydroformylation of alkenes (Scheme 1), especially catalysed by rhodium–phosphine complexes, is still one of the most extensively investigated processes of homogeneous catalysis.[1] Recent studies have focused on the synthesis of new catalytic systems, particularly water-soluble catalysts,[2] mechanistic investigations,[3] and the hydroformylation mediated synthesis of fine chemicals,[4] including asymmetric ones.[5]

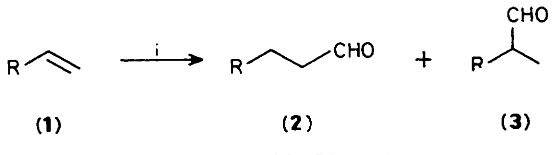
Much effort has been made to improve the regioselectivity of the hydroformylation of substituted alkenes (**1**) with special interest in linear (**2**) or branched (**3**) products, depending on the alkene used. From these studies, it appears generally that higher than stoicheiometric concentrations of phosphine enhance the regioselectivity at the expense of the activity although in the case of functionalized alkenes, no systematic study of the influence of the rhodium/phosphine ratio has been reported.

In the course of studies aimed at developing new catalytic systems involving phospholes (**4**),[6] we investigated the rhodium–phosphole complex-catalysed hydroformylation of alkenes and found that the readily available 1,2,5-triphenylphosphole ligand (TPP) (**5**) gave the best results and was by far superior to PPh_3.[7] Some phosphole complexes of cobalt have already been shown to be efficient for the hydroformylation of alkenes to alcohols.[8] With rhodium, the well-known 5-phenyl-5*H*-dibenzophosphole has been used in hydrogenation[9] and hydroformylation[10] of alkenes merely in mechanistic studies.[3,11] Only one patent claims the use of (**5**) as a diene in large excess in the hydroformylation of terminal alkenes using a quaternary system, *viz*. $Rh/PPh_3/Co$/diene.[12]

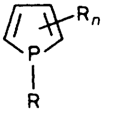
We have now found that the rhodium–TPP system-catalysed hydroformylation of alkenes is surprisingly not sensitive to the TPP/Rh ratio when it is $\geqslant 2$. Results of the hydroformylation of styrene (**1**) (R = Ph) catalysed by di-μ-chloro-tetracarbonyldirhodium $[Rh(CO)_2Cl]_2$ + *n*TPP (**5**) systems or by the $Rh(CO)Cl(TPP)_2$ complex[13] are reported in Table 1.

As usually observed, no by-products (hydrocarbons, alcohols, aldols *etc.*) were formed and the sum of the yields of 3-phenylpropanal (**2**) and 2-phenylpropanal (**3**) (R = Ph) represents the total amount of products. By performing runs at different stirring rates, we have checked that the reaction is not under diffusion control so that the results and the changes observed are accurate within the experimental errors.

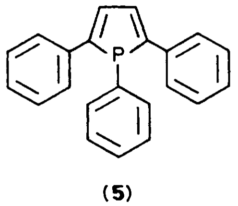
Several conclusions can be drawn from Table 1: (i) the regioselectivity is not affected when the TPP/Rh ratio varies from 1 to 20, and (ii) the yields of aldehydes do not change very much when the TPP/Rh ratio is 2 (runs 2—5). Some discrepancy between run 2 and run 3 for which the mixture $[Rh(CO)_2Cl]_2$ + 4 TPP and the complex $Rh(CO)Cl(TPP)_2$ are used respectively can be easily explained by considering that a small amount of $[Rh(CO)_2Cl]_2$ is not converted to the catalytically active species. Thus, it seems that a ratio of 2 is an optimum for these hydroformylation conditions. To confirm this, we performed a preliminary kinetic study under the conditions of run 1 and 3—5 by automatically monitoring the consumption of synthesis gas *vs*. time and plotting the styrene conversion *vs*. time.[14] This study revealed an induction period



Scheme 1. i, H_2/CO, Rh catalysts.



(**4**)



(**5**)

Table 1. Hydroformylation of styrene catalysed by Rh–TPP systems.[a]

Run	Catalyst	TPP/Rh	% Yield[b]	% Yield of (3)(R = Ph)[c] %	TOF[d]/min^{-1}
1	$[Rh(CO)_2Cl]_2$	1	57	83	0.65
2	$[Rh(CO)_2Cl]_2$	2	88	83	1.10
3	$Rh(CO)Cl(TPP)_2$	2	92	83	1.10
4	$[Rh(CO)_2Cl]_2$	5	98	82	1.20
5	$[Rh(CO)_2Cl]_2$	20	98	83	1.20

[a] [Rh] = 4.7×10^{-3} M; [styrene] = 1 M; [NEt_3] = 4.7×10^{-2} M in toluene; constant pressure of CO/H_2 1/1, 20 bar, 40 °C, 180 min. [b] Total yield of aldehydes based on the amount of styrene introduced as determined by g.c. [c] Selectivity to the branched aldehyde (**3**) (R = Ph) defined as (**3**)/(**2**) + (**3**) as determined by g.c. [d] TOF: turnover frequency defined as mol of substrate hydroformylated per mol of catalyst per minute.

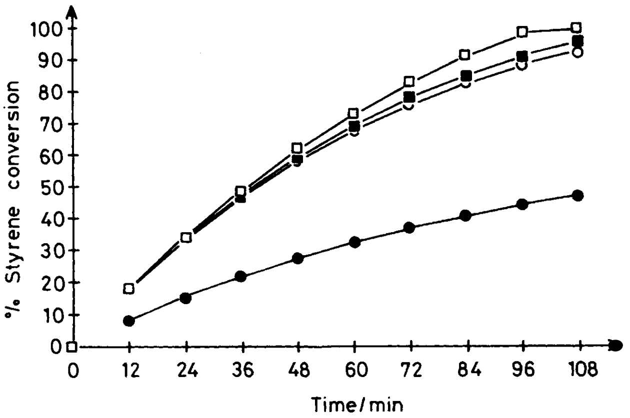


Figure 1. Conversion of styrene *vs.* time as a function of the TPP/Rh ratio; ● P/Rh = 1, ○ $Rh(CO)Cl(TPP)_2$, ■ P/Rh = 5, □ P/Rh = 20.

of *ca.* 5 min in all runs but also two important features of the catalytic system. First, at any time, the amount of styrene converted during run 3 (TPP/Rh = 2) is about twice that of run 1 (TPP/Rh = 1) suggesting that half of the rhodium charged is catalytically active in run 1. Secondly, when TPP/Rh ⩾ 2 (runs 3—5), the styrene conversion is the same for all runs, so confirming the idea that only two TPP ligands are needed in the active species. Moreover, the regioselectivity to the branched isomer (**3**) remains constant at 83% from 9—100% conversion of styrene.

These experimental observations are in favour of one, unique active species containing two and only two TPP ligands.

Comparative runs with PPh_3 instead of TPP under the same experimental conditions have shown that increasing PPh_3 concentration induces a sharp decrease in activity and a small increase in regioselectivity in the hydroformylation of styrene, a trend commonly observed in the hydroformylation of terminal alkenes. Similar experiments conducted with hex-1-ene instead of styrene led to the same results, *i.e.* neither the activity nor the regioselectivity of the hydroformylation depend on the TPP/Rh ratio when it is ⩾ 2. Furthermore, with ethyl acrylate as substrate, under these mild experimental conditions, this catalytic system gave rise to ethyl α-formylpropionate only.[7] This represents, for ethyl acrylate hydroformylation, the most efficient catalytic sytems involving a monophosphine yet discovered.[4]

Although we have been unable to isolate a rhodium-hydride complex containing a TPP ligand, we assume that the catalytically active species is the complex $HRh(CO)(TPP)_2$ and/or the complex $HRh(CO)_2(TPP)_2$ which are in equilibrium under carbon monoxide pressure and are not involved in association–dissociation equilibria of the TPP ligand. Therefore, these catalytic systems are the first systems involving a readily available monophosphine ligand, TPP, for which activity and selectivity are not influenced by the phosphorus/rhodium ratio.

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