Synergic effect of monophos ligands on hydroformylation

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Abstract: The hydroformylation of olefins, catalysed by rhodium complexes is largest scale industrial application of homogeneous catalysis.[1] The aldehyde products are extensively used as precursors to solvents, plasticizers, pharmaceuticals and other fine chemicals. In the last five decades, many ligands have been developed to improve the regioselectivity towards the higher value linear aldehydes. The hydroformylation catalyst based on Rh-PPh_3 complexes has found many applications.[2] Our focus has been on Rh catalysts based on pyrrolyl phosphines such as $PPyr_3$ which have strongly π-accepting properties.[3]
Keywords: Hydroformylation, Rhodium, Phosphines.

1. Introduction

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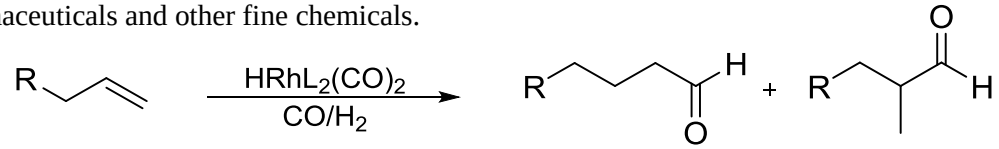

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2. Experimental

The 1-hexene substrate was filtered through alumina in order to remove impurities such as acetylene, water or peroxide which could affect the reproducibility of the catalysis. The hydroformylation experiments were performed in 50 mL Teflon reactor within a stainless steel (SS 316) autoclave. The autoclave was equipped with a separate reservoir, magnetic stirrer and a pressure transducer. In a glovebox, a toluene solution (1.5 mL) of [$Rh(CO)_{2(}$acac)] and ligands was prepared. The autoclave was placed under vacuum for 30 min. The solution was then injected in the high-pressure reactor under a nitrogen stream. Subsequently purged three times using 15 bar of syngas (CO/H_2 = 50/50). The solution was stirred at 90 °C for 1.5 h. In a separate reservoir a mixture of alkene (0.6 mL) and toluene (1 mL) was purged three times with 20 bar of CO/H_2. The substrate solution was then introduced into the autoclave using overpressure, and the autoclave was pressurized to a total pressure of 20 bar.

The hydroformylation reaction was stopped after a pressure drop of approximately 0.5 bar (10 Psi) was observed using a solution of tributylphosphite (1 mL) in toluene (1 mL). The autoclave was cooled rapidly using an ice-water bath and then depressurized. The experiments were performed in duplicate.

Two standard materials (decane 60 mg/mL and dodecane 15 mg/mL) were added at the end in order to monitor the reaction. The conversion, regioselectivity and amount of isomerized alkenes were determined by ^{1}H NMR spectroscopy and by GC-analysis of the reaction mixture.

3. Results and discussion

We have observed a synergic effect on the hydroformylation of 1-hexene using mixtures of $PPyr_3$ and PPh_3 ligands (see Figure 1).

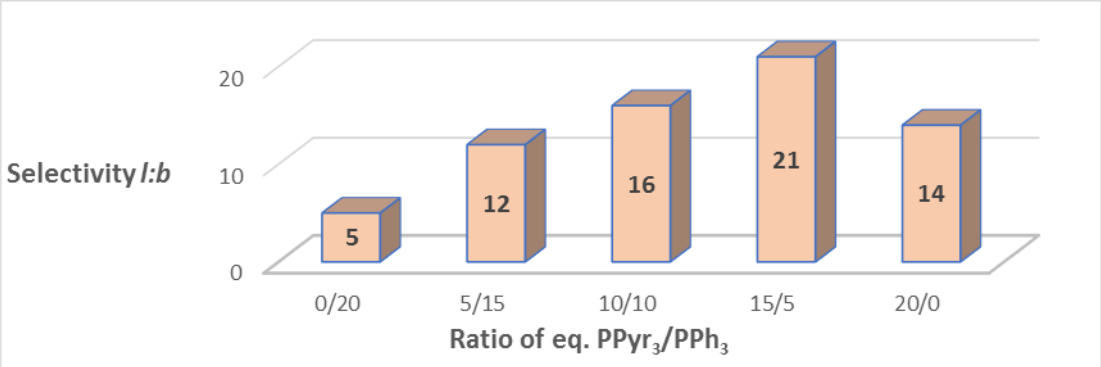

Figure 1. Rh-catalysed hydroformylation of 1-hexene with different ratios of $PPyr_3/PPh_3$.

The synergic effect of mixing phosphine ligands on Rh-catalysed hydroformylation has been expanded to the phosphorus ligands $P(3,5\text{-}(CF_3)_2C_6H_3)_3$ and $P(OC_6H_4CF_3)_3$ but the effect does not extend to bulky phosphine or phosphites.

An investigation of the effect mixed P-donors by NMR has shown that mixed ligand Rh complexes are certainly present at the end of the catalysis. Nonetheless, more work is required to elucidate the details of this reaction.

It has been shown that two unsymmetrical bidentate phosphine ligands did not show better hydroformylation activity or selectivity which may reflect the inflexibility of the xanthene and ethene backbones.

In an attempt to harness this synergic effect, the synthesis of the unsymmetrical bidentate ligand **1** (Figure 1, PyXantPhos) based on xanthene has been carried out. The hydroformylation catalysis results obtained with Rh/**1** complexes are presented below in Table1:

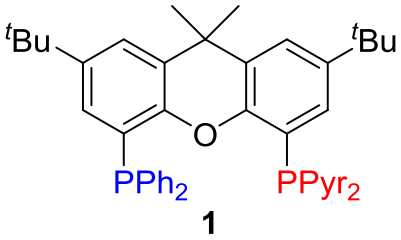

Figure 1. PyXantPhos ligand.

Ligand	*Conversion*	*Isomerisation*	*l:b*
PyXant	95%	18%	102
*Ligand **1***	**61%**	**9%**	**56**
XantPhos	19%	2%	44

Table 1. Hydroformylation of 1-hexene.

4. Conclusions

Using PPh_3 / $PPyr_3$ mixtures of ligands, a synergic effect on hydroformylation catalysis has been discovered. It appears that monodentates may be key to this effect since a heterobidentate analogue based on xantphos did not show an improvement in performance over the homobidentates.

Acknowledgements

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