

Letter

BINAS: A new ligand with outstanding properties in the hydroformylation of propylene

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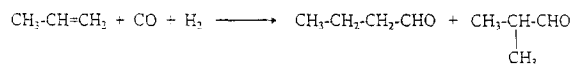
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The discovery of the hydroformylation reaction by Roelen in the laboratories of the Ruhrchemie AG — now Hoechst AG — in 1938 was followed by a period of nearly 35 years of strictly homogeneous application [1]. This was due to the nature of the metal hydrido-carbonyl complexes of cobalt, in the beginning, and of rhodium in the subsequent development.

The hydroformylation reaction is the catalytic conversion of olefins with carbon monoxide and hydrogen, with a mixture of linear and branched aldehydes being formed in an exothermic reaction. This is illustrated for propylene in the following equation:



Both the ‘naked’ hydridocarbonyls of Rh and Co mentioned are suffering from a limited selectivity with respect to the preferred linear

aldehydes. The problem could be reduced by the introduction of ligand modification of the metal carbonyl complexes by electron donating compounds, especially phosphines. Phosphine-modified rhodium carbonyls exhibit appreciable selectivity with respect to the formation of linear aldehydes and are thus the catalysts of choice today in most hydroformylation processes for propylene [2].

A new area in the propylene hydroformylation started with the application of the water-soluble threefold sulfonated triphenylphosphine (TPPTS) as a complex ligand, initiated by its discovery in the laboratories of Rhône-Poulenc in France [3]. Its implementation on an industrial scale after only two years of process development in the labs and the pilot plant was realized in 1984 by Hoechst, Werk Ruhrchemie in Oberhausen.

In the meantime, more than ten years of experience with the Ruhrchemie/Rhône-Poulenc process have been gathered, proving the excellent performance of the water-soluble (‘heterogenized’) catalyst system [4]. Numerous advantages of the biphasic system have been reported, concerning the chemical as well as technical suitability.

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As a result of the continual improvement of the hydroformylation processes and the catalyst system, also induced by reduced prices of oxo products — butanols, 2-ethylhexanol and di-2-ethylhexylphthalate — new, more active catalysts were developed in the last few years. Companies like Union Carbide and Eastman Kodak published in their patents numerous new oxo ligands for the homogeneous hydroformylation process [5].

For the Ruhrchemie/Rhône-Poulenc process, this implied the synthesis of new water-soluble phosphines, whereby the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl (BINAS) turned out to be one of the most active and selective ligands for the Rh catalysed propylene hydroformylation so far [6].

The synthesis of the unsulfonated precursor 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl (NAPHOS) — the first synthesis route was described by Kumada et al. — is based on 2-methylnaphthalene as feedstock [7] (Fig. 1).

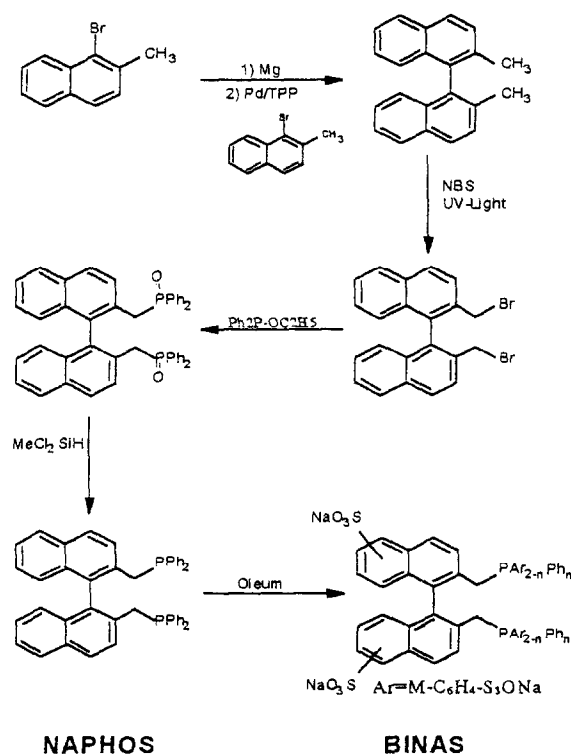


Fig. 1. Synthesis of BINAS.

In the first step of the synthesis route, 2-methylnaphthalene is brominated to 1-bromo-2-methylnaphthalene, which is dimerised by an aryl-aryl-coupling reaction of the bromo compound and the corresponding Grignard reagent using Pd/TPP as catalyst [7]a. The resulting 2,2'-dimethyl-1,1'-binaphthyl is brominated with N-bromosuccinimide (NBS) in chlorobenzene as solvent to 2,2'-bis(bromomethyl)-1,1'-binaphthyl [7]b. The subsequent Arbusov reaction with ethyl diphenylphosphinite leads to the dioxide of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl [7]c, which is reduced by methyl dichloro silane to NAPHOS [7]d. This process was successfully developed in a pilot plant scale in high yields.

In the last step of the BINAS synthesis, NAPHOS is sulfonated with fuming sulfuric acid with a sulfur trioxide content between 25–65%. Special sulfonation conditions are essential in order to avoid the formation of the sulfonated phosphine oxide components [8]. Herrmann and co-workers developed a new process for the sulfonation of phosphine ligands involving boric acid (H_3BO_3) [9]. By this method, a super acidic medium is generated, which forms the sulfonating agent $H_3SO_4^+$, that avoids oxidation of the phosphorus atom.

After hydrolysis of the sulfonation mixture, the sulfonated sodium salt species are isolated by the standard method developed for the production of TPPTS [10]. The resulting aqueous ligand solution is used without any further purification. Due to the structure of NAPHOS, which allows the sulfonation at various positions, BINAS is a mixture of numerous isomers. The numbers of isomers and their relative contents can be controlled by the sulfonation conditions.

The propylene hydroformylation using Rh/BINAS as catalyst system was developed in lab and in pilot plant scale [8]. In comparison to TPPTS as well as the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl (BI-SBIS) and the sulfonated triphenyl-dimethylphosphanorborna-diene (NORBOS), the

Rh/BINAS catalyst shows superior properties regarding activity and selectivity (n/i ratio) (Fig. 2).

Typical reaction conditions for BINAS are: temperature 110–130°C; pressure 20–60 bar;

P/Rh-ratio 10:1–50:1 and H₂:CO-ratio approx. 1:1. Using these conditions TOF rates of approx. 10000 h⁻¹ could be achieved.

Jumps in the activity from 16 mol aldehyde per mol Rh and minute to 160 mol for BINAS

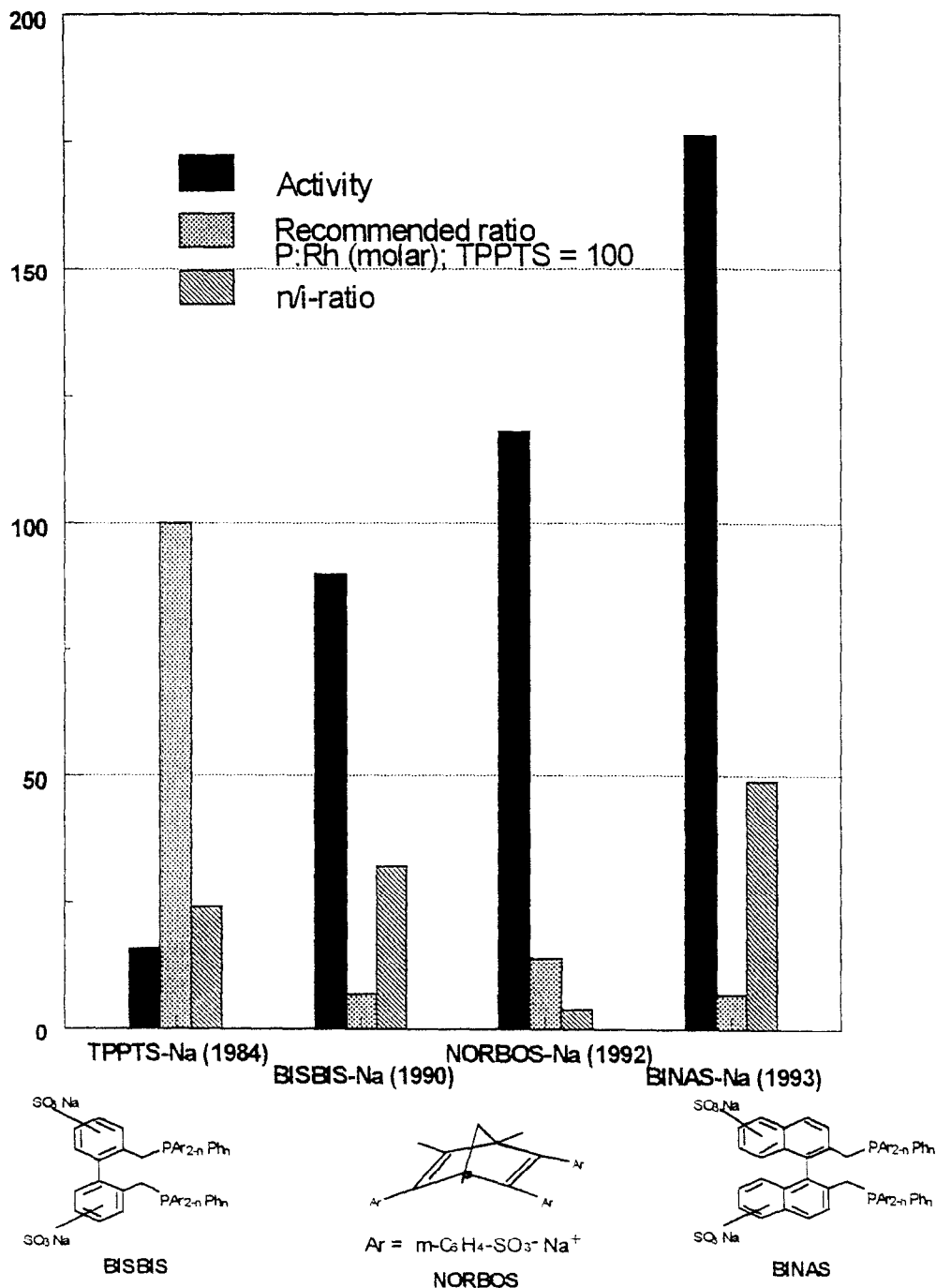


Fig. 2. New water-soluble P-ligands.

indicate the currently attainable activity levels. The n/i ratio in the propylene hydroformylation could be increased from 20:1 for TPPTS to 99:1 for BINAS.

This extremely high n/i ratio may be explained by the reaction mechanism proposed by Horvath [11] for the Rh/TPP catalysed system. In the case of excess of bidentate ligand only the trans-complex $\text{HRh}(\text{CO})\text{L}_2$ is being formed, which is the precursor for the linear aldehyde, compared to the monodentate $\text{HRh}(\text{CO})_2\text{L}$, which is the precursor for the branched aldehyde.

The extraordinary high activity of the complex $\text{HRh}(\text{CO})\text{L}_2$ based on bidentate ligands is not yet understood in detail. It may be explained by a very proper combination of ligand bite angle [12], rigidity [13], steric factors like trans-spanning according to Casey and Horvath [11,12] and electronic factors.

In contradiction to monodentate ligands like TPPTS, the P/Rh ratio in the hydroformylation

reaction can be reduced significantly by using the new more active bidentate phosphines like BINAS. Constant propylene conversion rates could be achieved during a test period of more than 2 months in the pilot plant at molar P/Rh ratios between 10–50:1 (Fig. 3).

In addition, the new catalyst ligand is very stable even at higher reaction temperatures up to 135°C.

Compared to monodentate ligands [4] BINAS also shows different behaviour due to the influence of the reaction pressure. In the range of 10 to 100 bar, the curve shows a maximum productivity (kg aldehyde per l catalyst solution and hour) at a medium pressure of about 25 bar and decreasing values with increasing pressure (Fig. 4).

After more than ten years of successful technical implementation of the Ruhrchemie/Rhône-Poulenc process with the first water-soluble catalyst Rh/TPPTS for the propylene hydroformylation, the sulfonated 2,2'-bis(di-

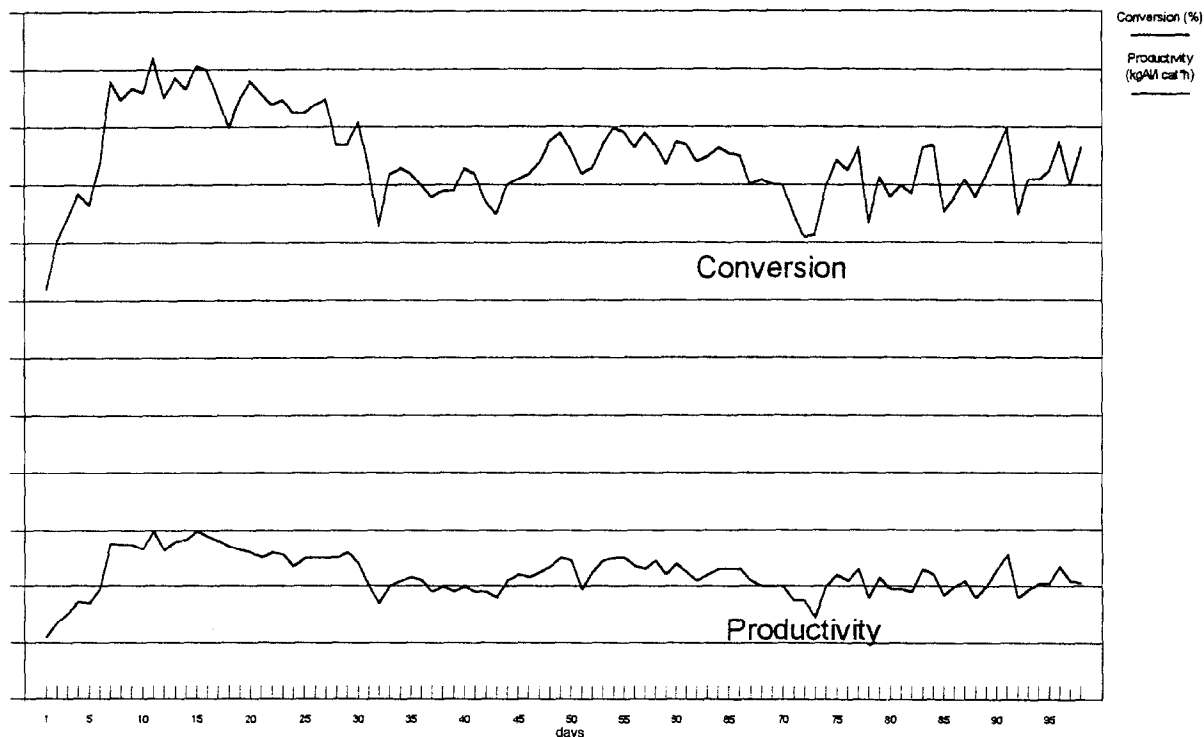


Fig. 3. Propylene hydroformylation using Rh/BINAS (T 125°C; p 25 bar; P/Rh 25:1).

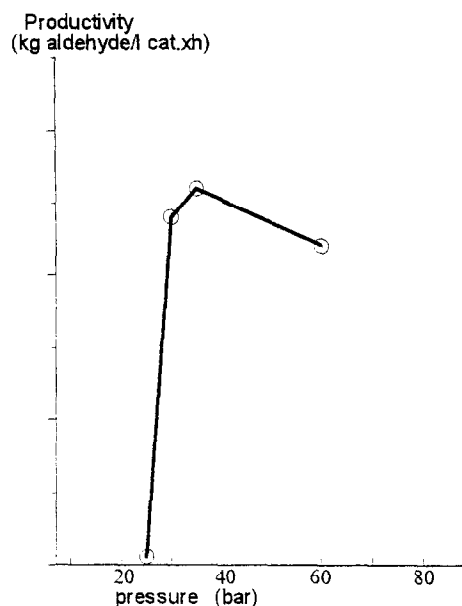


Fig. 4. Pressure dependence.

phenylphosphinomethyl)-1,1'-binaphthyl — BINAS — is a most excellent and technically reliable example for a bidentate ligand with superior properties. At low pressure and economically favourable P/Rh ratios, extremely high activities combined with an n/i ratio of up to 99:1 are achievable with the Rh/BINAS catalyst system.

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