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BINAS – synthesis and use of a new ligand for propylene hydroformylation

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Abstract

BINAS is a new, very efficient ligand for propylene hydroformylation. BINAS is made by the sulfonation of NAPHOS. Different synthetic routes to NAPHOS are discussed. A new two step synthesis starting from 2,2'-bis(bromomethyl)-1,1'-binaphthyl is described.

Keywords: BINAS; Phosphorus ligands; Propylene hydroformylation

1. Introduction

One of the most important reactions in industrial organic chemistry is the hydroformylation of olefins. In a transition metal complex catalysed process an olefin is reacted with carbon monoxide and hydrogen to form an aldehyde (Scheme 1). The so-called oxosynthesis was discovered by Otto Roelen in 1938 at the Ruhrchemie AG (now Hoechst AG) [1].

Originally, only cobalt carbonyl catalysts requiring high pressure were used. In the meantime rhodium hydridocarbonyl complexes involving phosphine ligands are the most important catalysts, especially for propylene hydroformylation [2].

With respect to catalyst recovery an easy separation of the catalyst and the oxoproduct was a major target in the further development of the oxosynthesis. A breakthrough in this area was achieved by the use of a water soluble catalyst allowing catalyst recovery via simple phase separation. The water solubility of the rhodium catalyst was achieved by use of the highly hydrophilic trifold sulfonated triphenylphosphine ligand, called TPPTS. This two phase hydroformylation process was discovered in the laboratories of Rhône-Poulenc in France by Kuntz et al. [3] and has been realized on an industrial scale by Ruhrchemie AG (now Hoechst AG) in Oberhausen, Germany [4].

The further development of this process led us to the evaluation of new water soluble phosphine ligands, especially bidentate phosphine ligands. In this paper we describe the synthesis and use of a new, very efficient, bidentate, water soluble ligand for propylene hydroformylation, called BINAS.

2. Results and discussion

BINAS is the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl, called NAPHOS. This bidentate phosphine was first described by Kumada et al. in 1974 [5]. They used a classical synthetic route starting with 1-bromo-2-methyl naphthalene, described in Scheme 1, route 3. In the first step an aryl–aryl coupling gives access to 2,2'-dimethyl-1,1'-binaphthyl. Side chain bromination and subsequent Arbusov reaction gives the NAPHOS dioxide, which is finally reduced to NAPHOS. In addition, two synthetic routes leading to NAPHOS are claimed in patents by the Eastman Kodak Company. One route starts with 2,2'-dimethyl-1,1'-binaphthyl, which is bis-metallated and reacted with chloro diphenylphosphine to NAPHOS [6] (Scheme 1, route 1). The other route gives NAPHOS via the reaction of 2,2'-bis(bromomethyl)-1,1'-binaph-

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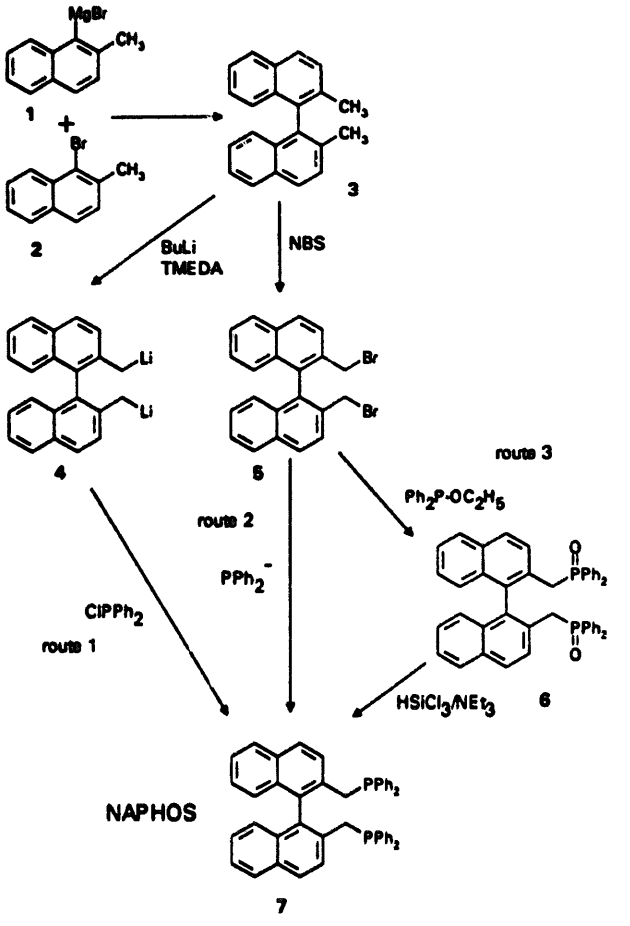
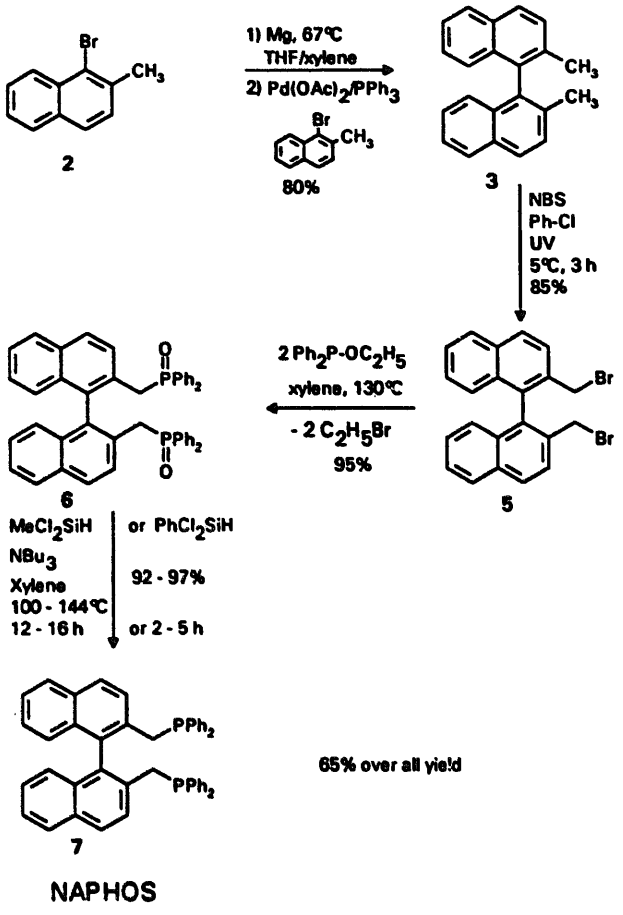


Scheme 1.

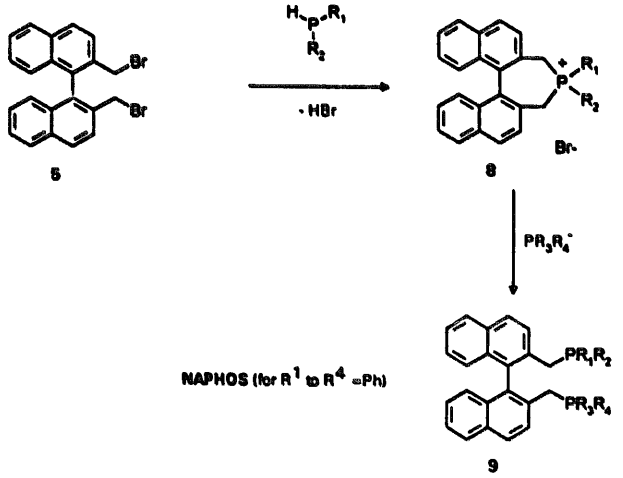


Scheme 2.

thyl with the diphenylphosphide anion (Scheme 1, route 2) [7].

The yield of the four step synthesis described by Kumada et al. is quite low, but could be improved significantly by us to an overall yield of about 65% (Scheme 2). The dimerisation is performed by an aryl–aryl coupling of the bromo compound and the corresponding grignard reagent with a palladium catalyst giving 2,2'-dimethyl-1,1'-binaphthyl **3** in 80% yield [8]. In the second step 2,2'-dimethyl-1,1'-binaphthyl **3** is brominated with N-bromo succinimide in chloro benzene at low temperature. In this way 2,2'-bromomethyl-1,1'-binaphthyl **5** is obtained in 90% yield [9]. This product can be used in the following Arbusov reaction between the dibromo compound and ethyl diphenylphosphinite without further purification. The Arbusov reaction is performed by slow addition of the diphenylphosphinite to a solution of the dibromo compound in xylene at 130°C. The NAPHOS dioxide **6** is obtained in 95% yield and very high purity [10]. In the last step NAPHOS dioxide **6** is reduced to NAPHOS **7** using methyl dichloro silane and tributylamine in xylene. Without aqueous workup NAPHOS is obtained in nearly quantitative yield and high purity (> 98%) [11].

Our attempts to find new routes to NAPHOS brought out another promising synthesis (Scheme 3). The reaction of 2,2'-dibromomethyl-1,1'-binaphthyl with diphenylphosphine results in the formation of a phosphepinium bromide **8**, a cyclic phosphonium salt [12]. The nucleophilic attack of the diphenylphosphide anion on the



Scheme 3.

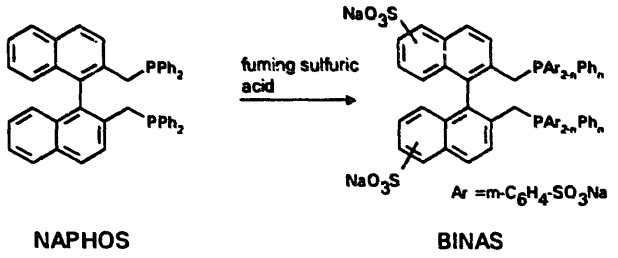
phosphonium salt gives NAPHOS in a ring opening reaction [13]. The yields of about 90% in the first step and about 75% in the second step are high. One of the main advantages of this process is the direct formation of NAPHOS, thereby eliminating the reduction step of the NAPHOS dioxide.

This process is quite similar to the process claimed by the Eastman Kodak Company (Scheme 1, route 2), in which 2,2'-dibromomethyl-1,1'-binaphthyl is reacted in one step with the diphenylphosphide anion to give NAPHOS. In our hands the Eastman Kodak process gives a very low yield of about 10%. As the main product we isolated the tert a phenyl diphosphine, which is obviously formed by a halogen metal exchange between the dibromo compound and the metal phosphide and subsequent combination of the so-formed halogen diphenylphosphine and the diphenylphosphide anion. We avoid this side reaction by a two step synthesis and the use of diphenylphosphine instead of diphenylphosphide in the first step. An equivalent alternative to diphenylphosphine is diphenyl trimethylsilyl phosphine.

In addition, this synthesis can be applied in a more general way than the routes described before, because the variation of the secondary phosphine used in the phosphonium salt formation gives access to a huge amount of different compounds [12]. In addition, the ring opening of the phosphonium salt with appropriate phosphide ions results in the formation of unsymmetrically substituted NAPHOS derivatives **9**. This is the only known method to synthesize these special kinds of NAPHOS derivative. The synthesis and application of some of these compounds will be described in another paper [14].

The sulfonation of NAPHOS is carried out in sulfuric acid using fuming sulfuric acid with a sulfur trioxide content between 25 and 65% as sulfonating agent. In order to avoid the oxidation of the three valent phosphorus atoms of the NAPHOS ligand, special conditions are required [15]. Besides the strict exclusion of oxygen the use of boric acid is helpful [16]. In such a sulfonating mixture $H_3SO_4^+$ is formed, which protects the phosphorus atom against oxidation. In an inert gas atmosphere NAPHOS is added to a mixture of boric and sulfuric acid. Afterwards fuming sulfuric acid is added dropwise at 0°C. After about 24–72 h at room temperature the reaction mixture is hydrolysed with water and worked up according to the procedure developed for the production of TPPTS [17]. In this way BINAS is obtained as a mixture of compounds with different sulfonation degrees. Each of these sulfonated species exists in regioisomers, which can easily be detected by HPLC. Fortunately the mixture obtained by the described process can be used without further purification in combination with rhodium in the hydroformylation process.

BINAS turned out to be one of the most active and selective ligands for the Rh-catalysed propylene hydroformylation. In comparison with other sulfonated phosphine ligands BINAS shows superior properties.



NAPHOS BINAS

The activity, measured in mol aldehyde per mol Rh per minute, could be increased significantly from 16 for TPPTS to approximately 160 for BINAS. In addition, the n/i ratio in the propylene hydroformylation could also be improved from 20:1 for TPPTS to 99:1 for BINAS.

The new Rh/BINAS catalyst system was tested in the pilot plant; constant propylene conversion rates could be achieved during a test period of more than 2 months at molar P/Rh ratios between 10–50:1.

After more than ten years of successful implementation of the Ruhrchemie/Rhône-Poulenc process with the first water soluble sulfonated Rh/TPPTS catalyst for propylene hydroformylation, the sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl (BINAS) is the most excellent and technically reliable example of a bidentate ligand with superior properties. At low pressure and economically favourable P/Rh ratios, extremely high activities combined with an n/i ratio up to 99:1 are achievable with the Rh/BINAS system, which additionally can be used as a "drop-in" catalyst in existing production units.

3. Experimental section

3.1. General

^{31}P-NMR spectra were obtained on a Bruker AM 360. 98% age phosphoric acid was used as external standard. Mass spectra were obtained on a MAT 95Q Finnigan MAT spectrometer using a glycerine matrix.

3.2. Materials

Commercially available diphenylphosphine and a 1 M potassium diphenylphosphide solution were used. DMF was dried with calcium hydride and distilled in vacuum prior to use. Toluene was dried with sodium hydride and distilled prior to use. The synthesis of 2,2'-bis(bromomethyl)-1,1'-binaphthyl is described in the literature [9].

3.3. (R,S)-4,4-diphenyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]phosphepinium bromide (8 with R^1 and R^2 phenyl)

Excluding air and moisture, 51.9 g (118 mmol) of (*R,S*)-2,2'-bis(bromomethyl)-1,1'-binaphthyl was dissolved in 400 ml of absolute toluene at room temperature. To this solution was added dropwise 22 g (118.2 mmol) of diphenylphosphine and the resulting reaction solution was heated to boiling for 8 h. After cooling, the colourless solid precipitated was filtered off and washed twice with 100 ml of toluene and 100 ml of low-boiling petroleum ether respectively. The colourless solid was then dried for 4 h in high vacuum. Yield 56.2 g (87%), m.p. > 300°C. ^{31}P-NMR spectrum (DMSO-d_6): δ = 42.5 ppm. FAB mass spectrum $[M-Br]^+$ 465.

3.4. 2 2'-Bis(diphenylphosphinomethyl)-1,1'-binaphthyl

Excluding air and moisture, 4.0 g (7.3 mmol) of (*R,S*)-4,4-diphenyl-4,5-dihydro-3H-dinaphth[2,1-c : 1', 2'-e]phosphepinium bromide was suspended in 40 ml of DMF. 7.4 ml (7.4 mmol) of a 1 M solution of potassium diphenylphosphide in THF was added dropwise. The resulting red solution was stirred at room temperature for 24 h. The DMF was then removed at 50°C 10^{-2} mmHg. The residue was taken up in 120 ml of toluene, 0.3 ml of water was added and the mixture stirred for 30 min. The precipitate separated out was filtered off (0.9 g) and the toluene removed at 50°C 10^2 mmHg. For purification, 10 ml of acetone was added to the residue and the resulting crystals were filtered off under an inert gas. 4 ml of iso-propanol was added to the acetone mother liquor and the mixture cooled at 0°C for several hours. The resulting precipitate was filtered off again. Yield 3.4 g (71%), m.p. 156°C. ^{31}P-NMR spectrum ($CDCl_3$): δ = 12.3 ppm.

3.5. Sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthyl

In an inert gas atmosphere, 7.6 g (123 mmol) of boric acid was dissolved at room temperature in 66.8 g of concentrated sulfuric acid, subsequently 10.1 g (15.5 mmol) of NAPHOS was added to this solution. After the phosphine was dissolved, 221.5 g of fuming sulfuric acid (containing 65% SO_3) was dropped slowly into the solution, maintaining the temperature in the range of about 10°C. After complete addition, the reaction mixture was stirred for 72 h at room temperature. The sulfonation mixture (306.0 g) was hydrolysed with 1300.0 g of water at a temperature below 20°C. After the addition of a mixture of 821.0 g of toluene and 82.1 g of triisooctylamine the two phase system was stirred for 1 h. In the next step, the organic phase was separated from the waste sulfuric acid phase. The organic toluene phase was re-extracted with an aqueous sodium hydroxide solution (1.5%) in order to form the corresponding sodium salts of the sulfonated BINAS species. A first fraction was isolated up to a pH value of 3.5, the pH value was measured with a standard type glass electrode. A second fraction was separated within the pH range 3.5–11.1. The second aqueous fraction with a boric acid content of 0.22 mmol is used in the hydroformylation reaction without any further purification.

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