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Inorganica Chimica Acta 223 (1994) 165–167

Inorganica Chimica Acta

Note

An improved synthesis of Ru(BINAP) type complexes

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Received by Editor 15 January 1994; received by Publisher 6 April 1994

Abstract

New synthetic methods for the preparation of Ru(BINAP) complexes have been developed. A major decomposition product, diphenylphosphinyl[1-(1′-naphthyl)-2-naphthyl)diphenylphosphine]ruthenium chloride, was identified and a simple, high yield synthesis of $Ru(BINAP)(OAc)_2$ was developed based on the understanding of this byproduct.

Keywords: Ruthenium complexes; BINAP complexes

1. Introduction

In recent years there has been increased interest in the chemistry related to Ru(BINAP) type complexes [1,2]. Among the various Ru(BINAP) complexes reported in the literature, $Ru(BINAP)(OAc)_2$ has attracted most attention owing to its high enantioselectivity in the asymmetric hydrogenation of prochiral olefins and β-ketoacids [1]. The original synthesis of $Ru(BINAP)(OAc)_2$ was based on two consecutive substitution reactions as outlined in Eqs. (1) [3] and (2) [4].

$$[Ru(COD)Cl_2]_n + BINAP + NEt_3 \xrightarrow[\text{toluene}]{\text{reflux}} [Ru(BINAP)Cl_2]_2(NEt_3) \quad (1)$$

$$[Ru(BINAP)Cl_2]_2(NEt_3) + NaOAc \xrightarrow[\text{t-BuOH}]{\text{reflux}} Ru(BINAP)(OAc)_2 \quad (2)$$

Generally, about 65–70% yield of the desired $Ru(BINAP)(OAc)_2$ was obtained. From a practical standpoint, it is desirable to develop a more convenient method for the preparation of $Ru(BINAP)(OAc)_2$ in higher yields. A convenient synthetic method for $Ru(BINAP)(OAc)_2$ may increase the catalyst's use by more chemists. Since BINAP is difficult to prepare [5], a high yield synthesis of $Ru(BINAP)(OAc)_2$ is particularly important for the development of commercial processes which require large quantities of the catalyst. Recently there have been publications of the in situ synthesis of Ru(BINAP) type catalysts from the reaction of BINAP with $Ru(COD)(OAc)_2$ [6], $[Ru(COD)Cl_2]_n$ [7], $[Ru(C_6H_6)Cl_2]_2$ [8] and $Ru(acac)_3$ [9]. The one-pot, two-stage synthesis reported by Noyori and coworkers was of particular interest [8b]. In this paper we wish to describe a simple and high yield synthesis of $Ru(BINAP)(OAc)_2$ from $[Ru(COD)Cl_2]_n$. We will also describe the isolation and characterization of a novel ruthenium diphenylphosphinyl complex resulting from the decomposition of Ru(BINAP) species.

2. Results and discussion

The reactions represented by Eqs. (1) and (2) were simple ligand substitutions. Based on the principles of coordination chemistry, it was possible to combine the two steps together to provide a more convenient method for the preparation of $Ru(BINAP)(OAc)_2$. In our initial attempt to develop a one-step synthesis of $Ru(BINAP)(OAc)_2$ from $[Ru(COD)Cl_2]_n$ and BINAP, we carried out the reaction of $[Ru(COD)Cl_2]_n$ with BINAP and sodium acetate in refluxed acetic acid (solvent) under an atmosphere of dinitrogen. As ex-

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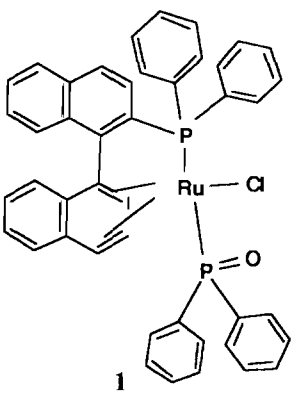
Elsevier Science S.A.
SSDI 0020-1693(94)03986-X

pected, fairly high yields (70–80%) of Ru(BINAP)-$(OAc)_2$ were obtained.

$$[Ru(COD)Cl_2]_n + BINAP + NaOAc \xrightarrow[HOAc]{reflux} Ru(BINAP)(OAc)_2 \quad (3)$$

This preliminary result was very encouraging because it offered a more convenient route to $Ru(BINAP)(OAc)_2$. In an attempt to further simplify this synthesis, we carried out the same reaction in the absence of sodium acetate. The purpose of omitting the sodium acetate was to simplify the isolation process. In the absence of other salts, the catalyst thus prepared may be obtained by simply distilling off the solvent. However, quite surprisingly the result turned out to be totally unexpected. According to the ^{31}P NMR of the product solution, at least five different unidentified species were obtained. Yet none of these was $Ru(BINAP)(OAc)_2$. A major species which accounted for about one-third to one-half of the products attracted most of our attention (species **1**: $^{31}P\{H\}$ NMR in acetone-d_6: P(1) = 58.2, P(2) = 71.2 ppm; J(P(1)–P(2)) = 56 Hz).

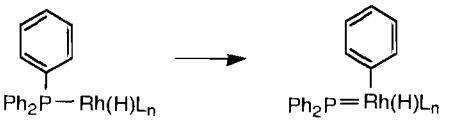
The mixed ruthenium complexes thus obtained were found to be an excellent catalyst for the asymmetric hydrogenation of 2-(6-methoxy-2-naphthyl)acrylic acid. To further improve this method of catalyst preparation, it was of interest to isolate, characterize, and then test **1** in the asymmetric hydrogenation of 2-(6-methoxy-2-naphthyl)acrylic acid. The rationale was that the formation of **1** should be optimized if this species was a good catalyst. On the other hand, if it was an inactive species, avoiding its formation should give a better catalyst. When an acetone/dichloromethane solution of the catalyst mixture was slowly evaporated under a dinitrogen atmosphere, single crystals of **1** were obtained. An X-ray diffraction study [10] of the complex revealed a rather surprising structure. One of the naphthyl phosphorus bonds in the BINAP ligand was ruptured and the resulting complex was a novel diphenylphosphinyl ruthenium species.



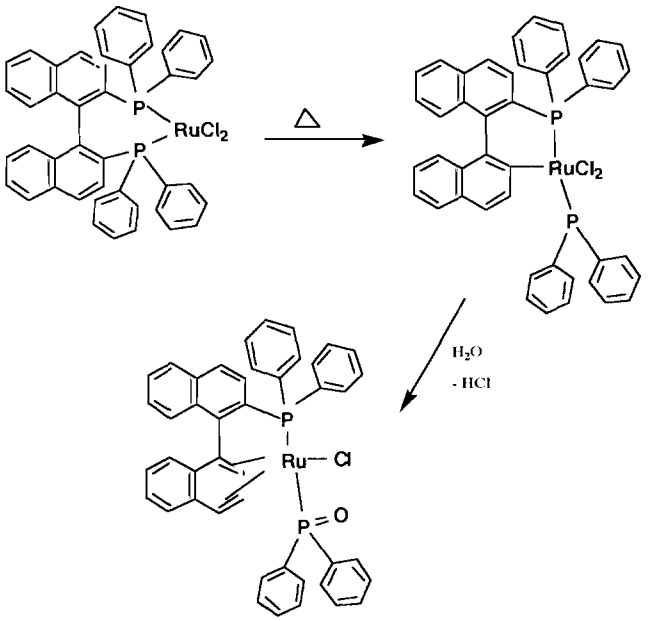
1

Complex **1** was found to be inactive in the asymmetric hydrogenation of 2-(6-methoxy-2-naphthyl)acrylic acid. At this stage it became clear to us that the formation of **1** should be avoided in an improved synthesis of the catalyst mixture.

While the formation of a diphenylphosphinyl ruthenium complex from the rupture of a BINAP ligand was unprecedented, the cleavage of phosphorus–carbon bonds in phosphine ligands had been reported before. For example, Abatjoglou *et al.* studied the cleavage of aryl–phosphorus bonds in rhodium carbonyl phosphine complexes and concluded that the cleavage was due to the oxidative addition of a P–C bond to the rhodium metal [11].



Analogously, it was possible to speculate a mechanism for the decomposition of the Ru(BINAP) complex via the oxidative addition of the naphthyl–phosphorus bond to the ruthenium center followed by hydrolysis. (The water of hydrolysis was from the acetic acid solvent.)



The rupture of the phosphorus–naphthyl bond via oxidative addition took place most likely when the ruthenium complex was in a highly unsaturated state. This reaction could be avoided by suppressing the formation of the unsaturated species. To accomplish this task, we used a large excess of an arene as a temporary coordinating agent to tie up the unsaturated species. Thus, by using toluene as a co-solvent in the reaction of $[Ru(COD)Cl_2]_n$ with BINAP, we found that the formation of **1** was indeed prevented. As expected, the resulting Ru(BINAP) catalyst mixture was twice as active as the mixture containing **1**.

The isolation and characterization of **1** also provided a good hint for our development of a high yield synthesis

method for $Ru(BINAP)(OAc)_2$. When $[Ru(COD)Cl_2]_n$ was allowed to react with BINAP and sodium acetate in a 1:1 mixture of acetic acid and toluene under an inert atmosphere (e.g. N_2) at about 85 °C, $Ru(BINAP)(OAc)_2$ was obtained in essentially quantitative yield. Interestingly, when toluene alone was used as solvent, essentially no reaction was observed. This might be due to the low solubility of $[Ru(COD)Cl_2]_n$ in toluene alone.

3. Experimental

3.1. Synthesis of $Ru(BINAP)(OAc)_2$

A Fischer-Porter bottle was charged with 0.1 g of $[Ru(COD)Cl_2]_n$, 0.23 g of S-BINAP, 2.0 g of anhydrous sodium acetate, and 50 ml of a 1:1 mixture of degassed toluene and glacial acetic acid under an atmosphere of dinitrogen. The mixture was stirred with a magnetic stirrer at about 85 °C for one week. The solvent was evaporated under reduced pressure. The product was extracted three times, each time with about 25 ml degassed dichloromethane, and the solvent of the combined extracts was evaporated under reduced pressure to give 0.29 g of a yellow product. ^1H and ^{31}P NMR studies of this material indicated that $Ru(BINAP)(OAc)_2$ was the only product.

Acknowledgements

A.S.C.C. thanks the National Science Council, R.O.C. for financial support of his collaborative research in Taiwan. Part of this work was carried out at Monsanto Corporate Research.

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