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Cationic η^6-Coordinated BINAP Rhodium Complexes with Benzene and Toluene

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Abstract. Two novel BINAP rhodium complexes containing η^6-coordinated arenes have been disclosed. Both have been characterized by X-ray analysis and NMR spectroscopy.

Introduction

The chelating diphosphine ligand BINAP was introduced into homogeneous catalysis by *Noyori* et al.[1] in 1980 and since then has proved to be a very successful chiral modifier.[2] An up-to-date compilation of results concerning its application in asymmetric hydrogenation promoted by cationic rhodium complexes can be found in Reference [3]. Recently very active cationic solvate complexes of the type [Rh(BINAP)(solvent)$_2$]-Anion have been characterized by X-ray analysis with the solvent being either methanol, tetrahydrofurane or acetone.[4] Such complexes were prepared by hydrogenation of the diolefin precatalysts [Rh(BINAP)(cod)]BF$_4$ (cod = 1,5-cyclooctadiene) or [Rh(BINAP)(nbd)]BF$_4$ (nbd = norbornadiene) in the corresponding solvents.[3] When hydrogenation of the same catalyst precursors was carried out in non-coordinating solvents, e.g. dichloromethane or dichloroethane, dimers resulted in which each BINAP acts as a bridging ligand through one of its phenyl moieties. The dimers have been characterized by X-ray analysis as well.[4]

BINAP is a classical seven-membered ring chelating ligand whose rhodium-substrate complexes are significant less stable than those containing typical five-membered ring chelating ligands like DPPE, Me-DuPhos and Et-DuPhos.[3] Rhodium complexes with the latter ligands may also coordinate arenes such as benzene or toluene in a η^6-fashion.[5] The apparent high stability of these rhodium-arene complexes might lead to deactivation phenomena in catalysis.[5–7]

This paper reports the preparation and full characterization of analogous rhodium-benzene and rhodium-toluene complexes containing the BINAP ligand.

Results and Discussion

When a tenfold excess of benzene was added to a solution of [Rh(BINAP)(MeOH)$_2$]BF$_4$ (0.01 mmol) in methanol (10 mL), a color change from yellow to light red occurred. By layering the solution with diethyl ether red crystals suitable for X-ray analysis were grown (Figure 1). The ^{31}P NMR spectrum of these crystals in deuterated dichloromethane shows that beside the known arene bridged dimer, a second species is present in solution[4] (^{31}P NMR in CD$_2$Cl$_2$, δ = 42.5 ppm; $J_{\text{Rh–P}}$ = 203.4 Hz; see spectrum in Supporting Information). The X-ray analysis documents the coordination of rhodium to the benzene ring.

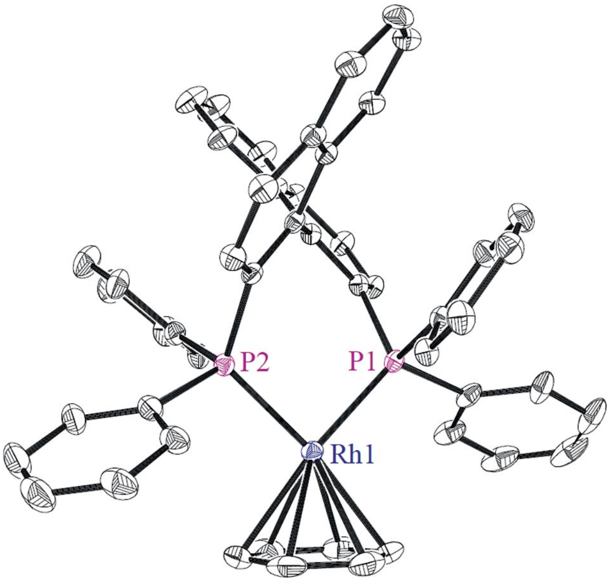

Figure 1. Molecular structure of the cation of [Rh(BINAP)(η^6-benzene)]BF$_4$; ORTEP, 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances and bond angles are summarized in Table 1. CCDC-861327.

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Analogue results were obtained by using toluene instead. The appropriate molecular structure is presented in Figure 2. The corresponding ^{31}P NMR spectrum (^{31}P NMR in CD_2Cl_2, $\delta = 42.6$ ppm; $J_{Rh–P} = 203.2$ Hz) is presented in the Supporting Information.

The data in Table 1 show that the relevant distances and angles in the two complexes are very similar.

Although rhodium arene complexes may be responsible for lower activity, asymmetric hydrogenations with cationic rhodium complexes in aromatic solvents have been described in the literature.[8] To what extent catalyst deactivation has to be considered depends on either the ratio of the stability constants of arene complexes and active catalyst complexes or, otherwise, on the ratio of the concentrations of arene and substrate.

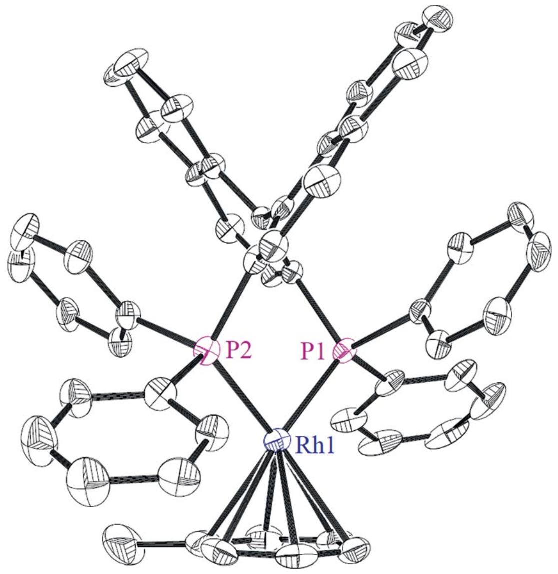

Figure 2. Molecular structure of the cation of [Rh(BINAP)(methyl-η^6-benzene)]BF_4; ORTEP, 30 % probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances and bond angles are summarized in Table 1. CCDC-861326.

Table 1. Selected distances /Å and bond angles /° of the isolated arene complexes.

Arene	distance /Å Rh–P	distance /Å Rh–η^6C	angle /° P–Rh–P
Benzene	2,231–2,241 (1)	2,288–2,367 (3)	89,86 (2)
Toluene	2,226–2,234 (2)	2,296–2,361 (4)	89,64 (4)

Conclusions

In summary it has been shown that, despite their less stability compared to analogues complexes bearing five-membered chiral chelating diphosphines, arene complexes [Rh(BINAP)(benzene)]BF_4 and [Rh(BINAP)(methyl-η^6-benzene)]BF_4 were successfully prepared, isolated and characterized by X-ray analysis.

Supporting Information (see footnote on the first page of this article): ^{31}P NMR spectra of the title compounds.

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