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Half-sandwich ruthenium(II) complexes containing a tricyclic β-iminophosphine ligand: Catalytic activity in Diels–Alder reactions

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Abstract

The diastereoselective κ^2-*P*,*N*-coordination of a chiral tricyclic β-iminophosphine ligand to the half-sandwich ruthenium(II) fragments $[RuCl(\eta^6\text{-arene})]^+$ (arene = C_6H_6, *p*-cymene, 1,3,5-$C_6H_3Me_3$, C_6Me_6), $[Ru(\eta^6\text{-}p\text{-cymene})(NCMe)]^{2+}$ and $[Ru(\eta^5\text{-}C_5H_5)(NCMe)]^+$ is described. The structures of the resulting mono- and dicationic cymene derivatives have been confirmed by X-ray crystallography. Studies on the catalytic activity of these Ru(II) compounds in Diels–Alder cycloaddition processes are also reported.

Keywords: Ruthenium; *P*,*N*-Ligands; Arene complexes; Cyclopentadienyl complexes; X-ray molecular structures

1. Introduction

The design and coordination chemistry of chelating ligands containing a mixed *P*,*N*-donor set have attracted a great interest in recent years [1]. In particular, the possibility of tailoring the steric and electronic properties of the different donor groups, as well as the hemilabile character shown by some of these ligands [2], has been widely exploited in homogenous catalysis [1]. In this context, we have recently described the zirconium-mediated synthesis of the unprecedented tricyclic β-iminophosphine ligand **1** starting from readily available 1-phenyl-2,3-dihydrophosphole (see Chart 1) [3]. Interestingly, this ligand presents chirality both at the hydrocarbonated skeleton and at the phosphorus atom itself, being accessible in enantiomerically pure form if the separated (R_P) or (S_P) enantiomers of the dihydrophosphole, instead of the racemic mixture, are used as starting materials [4]. The expected ability of **1** to act as a κ^2-*P*,*N*-chelating ligand was assessed in the high yield preparation of complexes $[PdCl_2(\kappa^2\text{-}P,N\text{-}\mathbf{1})]$, $[RuCl_2(\kappa^2\text{-}P,N\text{-}\mathbf{1})(PPh_3)]$ and $[Mo(CO)_4(\kappa^2\text{-}P,N\text{-}\mathbf{1})]$, the structure of the former being unequivocally confirmed by means of a single-crystal X-ray diffraction study [5]. We also note that, albeit with moderate enantioselectivities, enantiopure β-iminophosphine **1** has also found application in asymmetric Pd-catalyzed allylic substitution [4] and Ru-catalyzed hydrogenation processes [6].

Pursuing our studies aimed at exploiting the synthetic utility of the tricyclic β-iminophosphine **1**, in this paper we describe the synthesis, structural characterization and catalytic activity in Diels–Alder cycloadditions of the first half-sandwich ruthenium(II) compounds containing this *P*,*N*-donor ligand.

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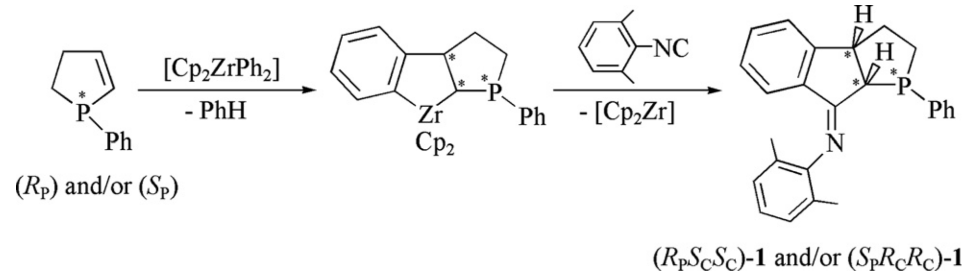
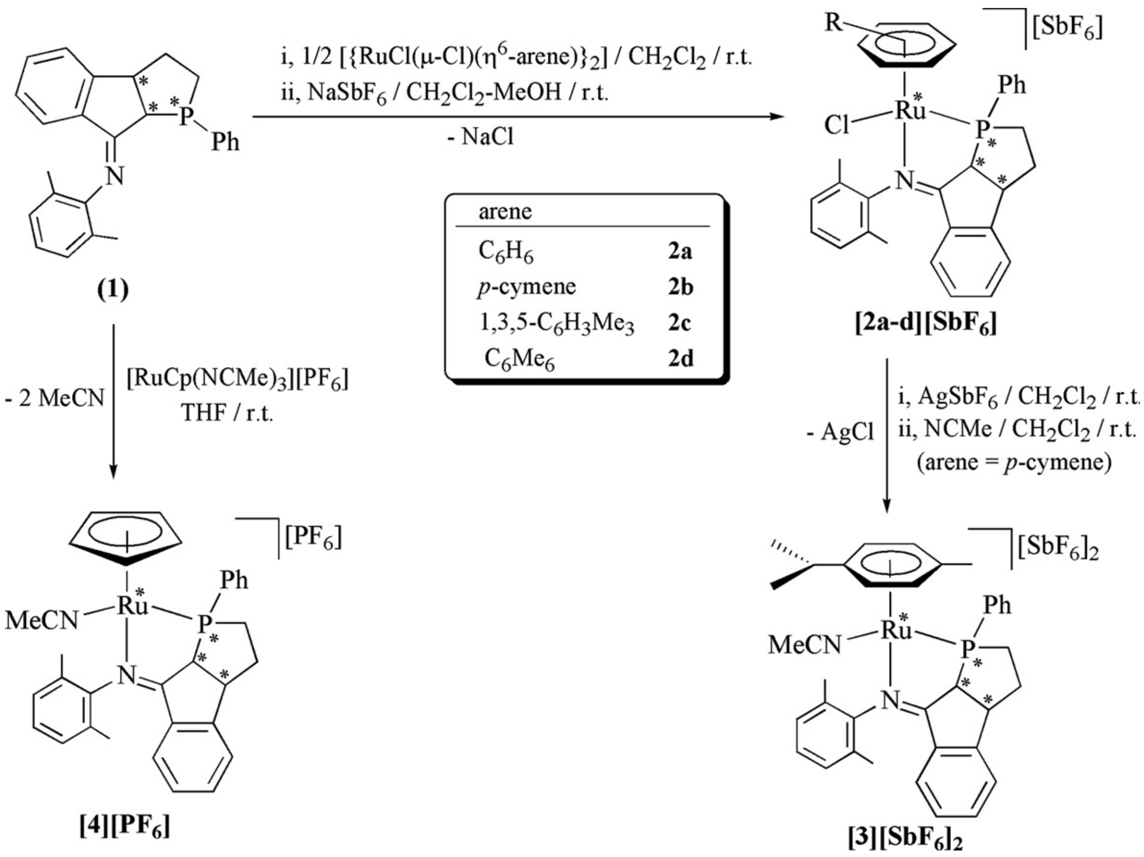


Chart 1. Synthesis of the tricyclic β-iminophosphine ligand **1**.



Scheme 1. Synthesis of half-sandwich ruthenium(II) derivatives containing ligand **1**.

2. Results and discussion

2.1. Synthesis and characterization of the half-sandwich ruthenium(II) compounds *[2a–d][SbF$_6$], [3][SbF$_6$]$_2$* and *[4][PF$_6$]*

The treatment of a dichloromethane solution of dimers $[\{RuCl(\mu\text{-}Cl)(\eta^6\text{-arene})\}_2]$ (arene = C_6H_6, *p*-cymene, 1,3,5-$C_6H_3Me_3$, C_6Me_6) [7] with a twofold excess of ligand **1**[1] leads to the selective formation of the cationic derivatives $[RuCl(\eta^6\text{-arene})(\kappa^2\text{-}P,N\text{-}\mathbf{1})][Cl]$ (**[2a–d][Cl]**), which have been isolated as the corresponding hexafluoroantimonate salts **[2a–d][SbF$_6$]** in 65–88% yield *via* classical Cl^-/SbF_6^- exchange using a methanolic solution of $NaSbF_6$ (Scheme 1). Compounds **[2a–d][SbF$_6$]** have been characterized by means of elemental analyses, conductance measurements, and IR and NMR (^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$) spectroscopies, all the data being fully consistent with the proposed structure (details are given in Section 4). Remarkably, the chelation of ligand **1**, which implies the generation of a new stereogenic centre on the ruthenium atom, takes place with complete diastereoselectivity as clearly assessed by the appearance of only one set of signals in their NMR spectra. In particular, the $^{31}P\{^1H\}$ NMR spectra display an unique singlet signal at δ 71.1 (**[2a][SbF$_6$]**), 71.4 (**[2b][SbF$_6$]**), 73.0 (**[2c][SbF$_6$]**) and 69.0 (**[2d][SbF$_6$]**) ppm. The coordination of the imine function

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[1] Used as the racemic $R_PS_CS_C/S_PR_CR_C$ mixture.