

## Cationic complexes of dirhodium(II) with 1,8-naphthyridine: Catalysis of reactions involving silanes

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### Abstract

The synthesis of cationic dirhodium(II) complexes by partial or total substitution of the acetate groups of  $[\text{Rh}_2(\text{OAc})_4]$  with different homoleptic neutral bidentate ligands has been attempted. The ligand 1,8-naphthyridine gave the best results: substitution of one as well as of all four acetate ligands is possible, giving rise to mono-, di- and tetra-cationic complexes. One of the resulting tetrasubstituted complexes has been structurally characterised and found to exhibit the expected lantern-shaped structure. All cationic complexes have been investigated as catalysts in different reactions involving silanes: promising results have been obtained, particularly in the silylformylation of alkynes.

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### 1. Introduction

Neutral dinuclear complexes of rhodium(II) are known to be catalytically active in a number of synthetically useful transformations [1]. The most popular reactions are metal-mediated decompositions of diazo derivatives, which upon formation of highly reactive metal carbene intermediates lead to cyclopropanations, insertions of the carbene moiety into C–H, C–C or heteroatom–H bonds, ylide formations or dipolar cycloaddition reactions; efficient asymmetric variants of many of these reactions have been developed as well [2,3]. Furthermore, neutral, electron poor dirhodium(II) complexes, such as dirhodium(II) perfluorocarboxylates do also efficiently catalyse many interesting reactions involving silanes, such as silane alcoholysis, hydrosilylations or silylformylations [4,5]. Despite the

recognised fundamental importance of the electrophilicity of these complexes in determining their activity and selectivity in catalytic reactions, it is quite surprising that up to now no systematic study on the catalytic efficiency of related *cationic* complexes has been carried out.

We have an ongoing research program aimed at the preparation of different kinds of cationic dirhodium(II) complexes and at the evaluation of their catalytic performance in reactions involving diazocompounds or silanes. Complexes of this kind can be prepared starting from simple dirhodium(II) acetate upon partial or complete substitution of the acetate moieties with neutral ligands. Although cationic dirhodium(II) complexes in which the acetate ligands have been substituted by coordinated solvent molecules, most commonly acetonitrile, are quite well known [6], much less common are examples in which the acetate ligands have been substituted by *bidentate* neutral ligands [7,8].

We have recently reported on cationic dirhodium(II) complexes with oxothioether molecules which exhibit a

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rather unusual bidentate O–S coordination, in which each bidentate ligand occupies one equatorial and one axial site in the complex; preliminary tests indicate that such complexes are promising catalysts of both the silylformylation and the hydrosilylation of 1-hexyne with dimethylphenylsilane [9].

We wanted to extend such investigations to cationic complexes in which the lantern-shaped structure of the  $[\text{Rh}_2(\text{OAc})_4]$  precursor is preserved. Such complexes can be obtained by partial or total substitution of the acetate moieties with homoleptic rather than heteroleptic neutral bidentate ligands, as demonstrated in the literature by the successful application of ligands based on 1,8-naphthyridine [7,8]. Thus, in this contribution we wish to report on the development of an improved synthesis of cationic dirhodium(II) complexes with 1,8-naphthyridine and on the results of a systematic study on the catalytic activity of these complexes in different model reactions involving silanes, such as silylformylations, hydrosilylations and silane alcoholysis. Furthermore, preliminary results on our attempts to generalise this strategy for the synthesis of cationic dirhodium(II) complexes to other neutral bidentate ligands will be presented.

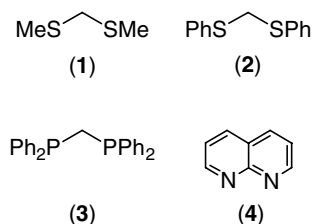
## 2. Results and discussion

In the course of our study, we have investigated four different potential neutral bidentate ligands of N–N, P–P and S–S types, which are reported in Scheme 1.

The outcome of this investigation was that, in the case of P–P and S–S ligands, the bidentate ligands gave upon reaction with  $\text{Rh}_2(\text{OAc})_4$  in toluene at room temperature simple coordination to the free apical positions of the metal precursor, yielding poorly soluble coordination polymers. Upon forcing the reaction conditions by prolonged heating of the resulting products in acetic acid in order to labilise the acetate ligands and favour their substitution, the coordination polymer derived from (1) dissolved, yielding however a mixture of products of common stoichiometry  $[\text{Rh}_2(\text{MeSCH}_2\text{SMe})_2(\text{OAc})_4]$ , in which the ligand (1) probably occupies different coordination sites. In contrast, the coordination polymer derived from ligand (2) remained virtually insoluble, whereas in the case of the P–P ligand (3) the mononuclear rhodium(III) complex  $[\text{Rh}(\text{P–P})(\text{OAc})_3]$  was formed, in accordance to previous observations by Cotton et al. with the same diphosphine ligand but using a different synthetic procedure [10]. The only

exception to this general behaviour was observed with the 1,8-naphthyridine ligand (4). When  $\text{Rh}_2(\text{OAc})_4$  was reacted at room temperature with one or two equivalents of (4), no product derived from simple ligand addition was observed. Instead, a well-defined cationic complex was formed stemming from the neat substitution with a 1,8-naphthyridine ligand of one acetate ligand, which then acted as counterion (Scheme 2). Remarkably, no addition of a strong acid such as HCl, as reported, for example in Ref. [7], was necessary in order to allow the reaction to proceed. The structure of the complex was confirmed spectroscopically: the  $^1\text{H-NMR}$  spectrum clearly reveals the presence of two kinds of bridging acetate ligands in a 2:1 ratio, as well as of an acetate counterion. Only the monosubstituted product (5) was formed, even in the presence of excess ligand. The substitution process could be pushed further by forcing the reaction conditions. Thus, by reacting  $\text{Rh}_2(\text{OAc})_4$  with four equivalents of (4) in acetic acid at reflux, complete substitution of the acetate ligands occurred, with formation of complex (6). The resulting complex was however only dicationic, in that two acetate ligands remained in the coordination sphere of the complex by occupying its apical positions, the other two acting as counterions, as confirmed by NMR analysis. Since the apical positions of dirhodium(II) complexes are usually their catalytically active sites, we expected their occupation by acetate ligands to have a negative effect on their reactivity. Therefore, we tried to remove the apical acetates by anion exchange with  $\text{NaBPh}_4$ . Such treatment only caused the substitution of the acetate counterions with two  $\text{BPh}_4^-$  anions, but left the coordinated acetates untouched, yielding complex (7). The apical acetates could finally be removed by treatment with Meerwein's salt triethyloxonium tetrafluoroborate, which ethylated them yielding the tetracationic complex (8).

The structure of complex (7)· $10\text{CH}_3\text{CN}$  was determined by X-ray diffraction methods. In the crystals, cations  $[\text{Rh}_2(\text{OAc})_2(\text{Naft})_4]^{2+}$  (Naft = 1,8-naphthyridine), anions  $\text{BPh}_4^-$  and solvent molecules  $\text{CH}_3\text{CN}$  were found. An ORTEP view of the cation is shown in Fig. 1, together with the atomic labelling scheme. A selection of the most important bond distances and angles is listed in Table 1. The cationic complex is centrosymmetric with the inversion center on the midpoint of the Rh–Rh bond. The coordination of each Rh atom is essentially octahedral, with four nitrogen atoms of the four naphthyridine ligands lying on the equatorial plane, the acetate ion and the other Rh atom on the apical sites completing the octahedral coordination. The Rh–Rh bond distance of 2.448(1) Å falls within the expected range for dirhodium(II) complexes and is slightly longer than that reported for the complex  $[\text{Rh}_2(\text{OAc})_4(\text{H}_2\text{O})_2]$  [11]; the four naphthyridine ligands bridge the Rh atoms through the N atoms with Rh–N bond lengths ranging from 2.050(3) to 2.077(3) Å, typical for  $\text{N}_{(pyridil)}-\text{Rh}$  coordination [12]. The acetate anions are bound to the Rh through an oxygen atom (Rh1–O1 bond length of 2.297(2) Å and O1–Rh1–Rh1' bond angle of 173.94(5)°).



Scheme 1. Sketch of the employed bidentate ligands.

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