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Rhodium assisted C—H activation of N-(2'-hydroxyphenyl)benzaldimines. Synthesis, structure and electrochemical properties of a group of organorhodium complexes

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Abstract

Reaction of a group of N-(2'-hydroxyphenyl)benzaldimines, derived from 2-aminophenol and five *para*-substituted benzaldehydes (the *para* substituents are OCH₃, CH₃, H, Cl and NO₂), with [Rh(PPh₃)₃Cl] in refluxing toluene in the presence of a base (NEt₃) afforded a family of organometallic complexes of rhodium(III). The crystal structure of one complex has been determined by X-ray crystallog-raphy. In these complexes the benzaldimine ligands are coordinated to the metal center, via dissociation of the phenolic proton and the phenyl proton at the *ortho* position of the phenyl ring in the imine fragment, as dianionic tridentate C,N,O-donors, and the two PPh₃ ligands are trans. The complexes are diamagnetic (low-spin d⁶, S = 0) and show intense MLCT transitions in the visible region. Cyclic voltammetry shows a Rh(III)—Rh(IV) oxidation within 0.63–0.93 V vs SCE followed by an oxidation of the coordinated benzaldimine ligand. A reduction of the coordinated benzaldimine is also observed within -0.96 to -1.04 V vs SCE. Potential of the Rh(III)—Rh(IV) oxidation is found to be sensitive to the nature of the *para*-substituent.

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1. Introduction

Utilization of transition metals in promoting useful chemical transformations of organic substrates has been of considerable current interest [1]. Such transformations usually proceed via a C—H activation of the organic substrate [2], leading to the formation of a reactive organometallic intermediate, which then undergoes further reactions to yield the final product. Transition metal mediated C—H activation of organic molecules is therefore of significant importance and the present work has originated from our interest in this area [3]. For the present study, a group of five Schiff base ligands, viz. N-(2'-hydroxyphenyl)benzaldimines (1), derived from *para*-substituted benzaldehydes

and 2-aminophenol, have been selected as the target molecules for C-H activation and rhodium has been selected as the transition metal for promoting the C-H activation. These ligands have two potential donor sites, the phenolate-oxygen and the imine-nitrogen, and hence are expected to bind to metal ions, via dissociation of the phenolic proton, as bidentate N,O-donors forming five-membered chelate ring (2). In view of the closeness of the pendent phenyl ring to the metal center in 2, C-H activation at the ortho position of the phenyl ring leading to the formation of a cyclometallated species (3) appears to be a possibility. With the intention of inducing the said C-H activation of the N-(2'-hydroxyphenyl)benzaldimines (1), their reaction has been carried out with the Wilkinson's catalyst, viz. [Rh(PPh₃)₃Cl]. This particular complex has been picked up as the rhodium starting material for this reaction because of its demonstrated ability to promote C-H

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activation, as well as to accommodate tridentate ligands [3a,4]. Reaction of the N-(2'-hydroxyphenyl)benzaldimines (1) with [Rh(PPh₃)₃Cl] has indeed afforded a family of organorhodium complexes, where the benzaldimines are coordinated to the metal center as in 3. The present report deals with the chemistry of these organorhodium complexes, with special reference to their formation, structure and, spectral and electrochemical properties.



2. Results and discussion

2.1. Synthesis and characterization

Reactions of the N-(2'-hydroxyphenyl)benzaldimines (1) with [Rh(PPh₃)₃Cl] proceed smoothly in refluxing toluene in the presence of triethylamine to afford a group of pinkish-orange [5] complexes in decent yields. The preliminary characterization (microanalytical, magnetic susceptibility, IR, ¹H NMR) data of these complexes indicate that in each of them one benzaldimine, two triphenylphosphines and a chloride are coordinated to rhodium. To find out the stereochemistry of the complexes as well as to ascertain the coordination mode of the benzaldimines in them, structure of a selected member of this family, viz. that obtained from the reaction with N-(2'-hydroxyphenyl)-4-methoxybenzaldimine $(1, R = OCH_3)$ has been determined by X-ray crystallography. The structure (Fig. 1) shows that the benzaldimine is coordinated to rhodium as a dianionic tridentate C,N,O-donor (3). The coordinated chloride shares the same equatorial plane with the tricoordinated benzaldimine ligand and the metal center, while the two PPh₃ ligands have taken up the remaining two axial positions and hence they are mutually trans. Rhodium is thus sitting in a CNOP₂Cl environment, which is significantly distorted from ideal octahedral geometry, as reflected in the bond parameters around the metal center. The Rh-C, Rh-N,



Fig. 1. View of the 4-OCH₃ molecule.

Rh—P and Rh—Cl distances (Table 1) are all quite normal [3a,4b] and so are those within the CNO-coordinated benzaldimine. However, the Rh—O bond is notably longer than normal and this elongation may be attributed to the strain developed due to the formation of two adjacent five-membered chelate rings by the benzaldimine. As all the five complexes in this family (4) have been prepared similarly and they display similar spectral and electrochemical properties (vide infra), the other four 4-R ($R \neq OCH_3$) complexes are assumed to have a similar structure as 4-OCH₃.



Table 1		
Selected bond lengths (Å) a	nd bond angles (°) for	complex 4-OCH ₃

Bond lengths (Å)			
Rh(1)-C(75)	1.996(9)	C(72)-N(71)	1.345(11)
Rh(1) - N(71)	1.987(7)	C(87)-N(71)	1.413(11)
Rh(1)-O(81)	2.167(7)	C(82)-O(81)	1.329(10)
Rh(1)-P(1)	2.387(4)		
Rh(1)-P(2)	2.378(4)		
Rh(1)— $Cl(3)$	2.387(4)		
Bond angles (°)			
C(75)— $Rh(1)$ — $O(81)$	162.5(2)	C(75)-Rh(1)-N(71)	82.0(3)
P(1) - Rh(1) - P(2)	176.24(10)	N(71)-Rh(1)-O(81)	80.6(2)
N(71)— $Rh(1)$ — $Cl(3)$	179.83(16)		

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