Journal of Organometallic Chemistry 694 (2009) 3401–3408

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Reactions of 2-(arylazo)aniline with ruthenium substrates: Isolation, characterizations and reactivities of delocalized diazoketiminato and orthometallated Ru(II) chelates

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A R T I C L E I N F O

Article history:
Received 30 April 2009
Received in revised form 22 June 2009
Accepted 26 June 2009
Available online 1 July 2009

Keywords:
2-(Arylazo)aniline
Ruthenium
Cycloruthenation
Redox
Hydrogen transfer reaction

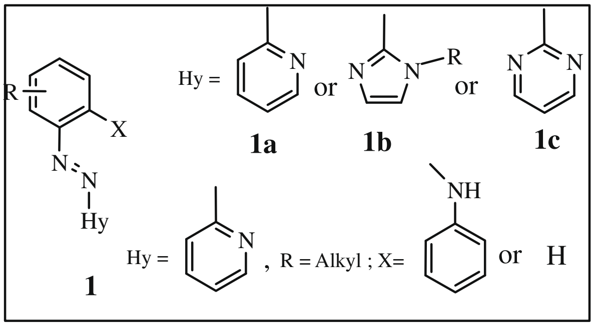
A B S T R A C T

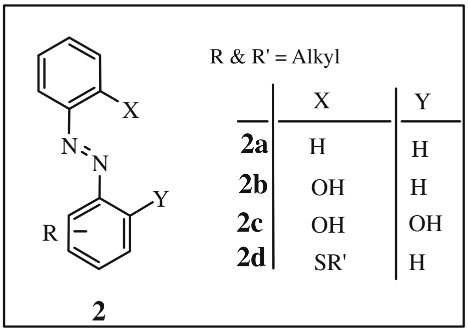
Reactions of 2-(arylazo)aniline, HL-NH_2 [H represents the dissociable protons upon complexation and HL-NH_2 is p-$RC_6H_4N{=}NC_6H_4$-NH_2; R = H for HL^1-NH_2; CH_3 for HL^2-NH_2 and Cl for HL^3-NH_2] with Ru(H)(CO)$(PPh_3)_3$Cl and $Ru(CO)_3(PPh_3)_2$ afforded products of compositions [(HL-NH)Ru(CO)Cl$(PPh_3)_2$] and [(L-NH)Ru$(PPh_3)_2$(CO)], respectively. All the complexes were characterized unequivocally. The X-ray structures of the complexes **4c** and **5c** have been determined. The cyclic volatammograms exhibited one reversible oxidative response in the range of 0.56–0.16 V versus SCE for [(L-NH)Ru$(PPh_3)_2$(CO)] and a quasi reversible oxidative response within 0.56–0.70 V versus SCE for [(HL-NH)Ru(CO)Cl$(PPh_3)_2$]. The conversion of ketones to corresponding alcohols has been studied in presence of newly synthesized ruthenium complexes.

1. Introduction

Research in the area of coordination chemistry of ruthenium incorporating various kinds of ligands has upsurged in recent years due to the fascinating reactivities exhibited by the resultant complexes [1–4]. Studies on the chemistry of ruthenium complexes with azo ligands have been ongoing and several interesting results, related to electron transfer reaction [5–26], metal–carbon bond formation [14,22,23,25,26], aromatic ring amination [16–18], isomerism [7,8,24], cytotoxicity toward cancer cells [5–11] and application in catalytic transformations [25,26], were reported. The π-acidic nature of azo (–N=N–) function was indicated to be one of the reasons for fascinating properties of such ruthenium complexes [5–26]. As a consequence we expected that the appropriately designed azo ligands can dictate the properties of ruthenium complexes to originate new and more attractive results.

In general, the azo ligand systems may be divided into two categories: (i) arylazo heterocycles, **1** and (ii) associates of azobenzene moiety, **2**. Among these ligands most widely studied system is 2-arylazo pyridine (AAP), **1a**. AAP ligands bind to the ruthenium center in bidentate fashion (N,N) affording different types of isomeric complexes [7,8]. It was also reported that the metal mediated aryl ring amination of AAP ligand lead to the formation of tridentate (N,N,N) ligands [16–18], Aryl ring thiolation was studied in ruthenium complexes of AAP to obtain new complexes where the ligands bind with tridentate (N,N,S) mode [20], Several studies





	X	Y
2a	H	H
2b	OH	H
2c	OH	OH
2d	SR'	H

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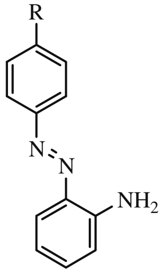
doi:10.1016/j.jorganchem.2009.06.038

related to electron transfer behavior [5–26], optical properties [12,13] and cytotoxic behavior of ruthenium AAP complexes [5–11] are worthwhile to mention. Isomerism and redox behavior of ruthenium complexes of aryl azo imidazole, **1b**, ligands were studied to a considerable extent [24].

Chemistry of ruthenium complexes with azobenzene and related ligands was not studied as much as that of arylazo heterocycle complexes. A few ruthenium complexes of azobenzene and related ligands were prepared and have been described to have interesting properties. The complexes of 2-arylazo phenols, **2b**, were demonstrated to exhibit C–H activation [22,23,25,26], C–C activation [23], C–C coupling [22] and catalytic hydrogen transfer reactions [25,26]. Viewing this, we intended to study the chemistry of ruthenium with new azobenzene related ligands. For the present purpose, we have utilized 2-(arylazo)aniline, HL-NH$_2$, **3**, ligand for the preparation of different types of ruthenium chelates.



R= H for HL^1-NH$_2$ (**3a**); CH$_3$ for HL^2-NH$_2$ (**3b**); Cl for HL^3-NH$_2$ (**3c**)

3

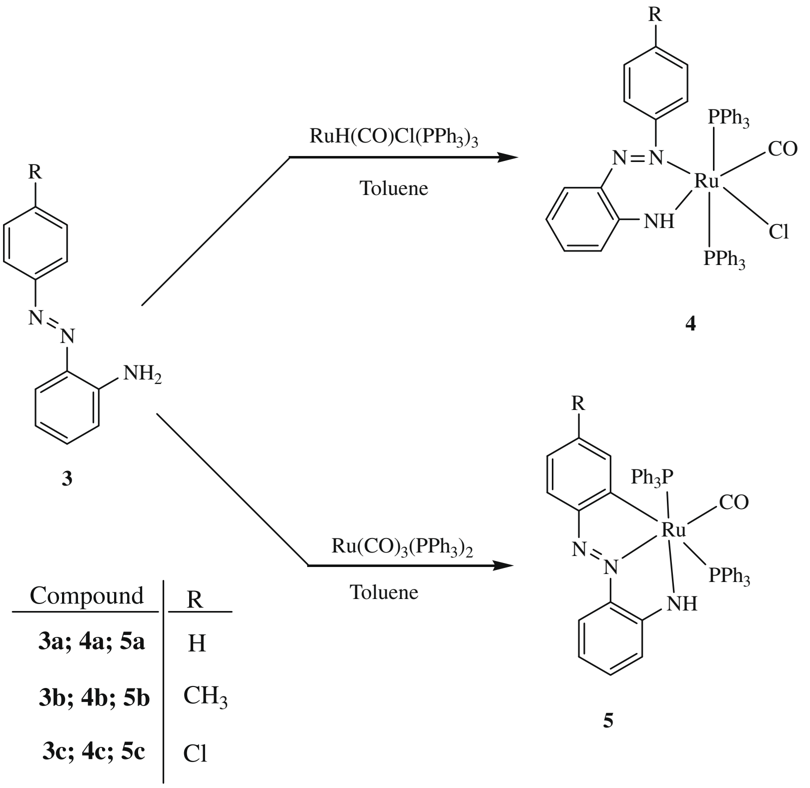
Herein we report the reaction of 2-(arylazo)aniline, **3**, with two ruthenium substrates. It has been shown that the different products were formed upon varying the ruthenium substrates. Orthometallated ruthenium (II) complexes were obtained from Ru(0) substrate. The products were characterized unequivocally. Redox properties and conversion of ketones in presence of new ruthenium complexes have been described.

2. Results and discussion

2.1. Complex formation

Reactions of HL-NH$_2$ with RuH(CO)Cl(PPh$_3$)$_3$ in refluxing toluene in anaerobic condition afforded a blue complex. Dissociation of one amino proton of HL-NH$_2$ and one hydride from RuH(CO)Cl(PPh$_3$)$_3$ gave rise to the formation of blue and non conducting complex [(HL-NH)Ru(CO)Cl(PPh$_3$)$_2$], **4** (Scheme 1). The anionic [HL-NH]$^-$ ligand coordinated the metal center forming a six membered diazoketiminato chelate. Therefore, formally the elimination of one equivalent of hydrogen ($H^+ + H^- \rightarrow H_2$) in addition to dissociation of a PPh$_3$ ligand was believed to be the essential criterion to form the complex **4.** Previously, we reported that the reaction of HL-NH$_2$ with RhCl(PPh)$_3$, where oxidative addition of the ligand led to the formation of cyclometallated Rh(III) complex [27]. By analogy we considered that an oxidative addition on ruthenium center may also afford the cyclometallated complex.

Hence, we assumed that a Ru(0) substrate may bind with HL-NH$_2$ giving rise to Ru–C bond formation. Indeed, reactions of the ligand system 2-(arylazo)aniline, with Ru(CO)$_3$(PPh$_3$)$_2$, afforded the cyclometallated complexes as given in **5**. The [(L-NH)Ru(PPh$_3$)$_2$(CO)], **5**, complexes are a new family of orthometallated complexes of Ru(II) [Eq. (1)]. Besides the elimination of one of the amino protons, an aryl proton of HL-NH$_2$ was dissociated from the pendant aryl ring during orthometallation. Two electron oxidation of Ru(0) center and concomitant dissociation of two protons from the ligand is formally consistent with the release of $2H^+ - 2e^-$. Reactions of HL-NH$_2$ with Ru(CO)$_3$(PPh$_3$)$_2$ in inert condition or in



Compound	R
3a; 4a; 5a	H
3b; 4b; 5b	CH$_3$
3c; 4c; 5c	Cl

Scheme 1.