

Relating catalytic activity and electrochemical properties: The case of arene–ruthenium phenanthroline complexes catalytically active in transfer hydrogenation

Petr Štěpnička^{a,*}, Jiří Ludvík^b, Jérôme Canivet^c, Georg Süß-Fink^{c,*}

^a Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, CZ-12840 Prague 2, Czech Republic

^b J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

^c Institut de Chimie, Université de Neuchâtel, Case postale 2, CH-2007 Neuchâtel, Switzerland

Received 22 November 2005; received in revised form 14 February 2006; accepted 23 February 2006

Available online 3 March 2006

Abstract

The electrochemical properties of cationic complexes $[(\eta^6\text{-arene})\text{Ru}(\text{N}\cap\text{N})\text{Cl}]\text{Cl}$ (arene/ $\text{N}\cap\text{N}$ = $\text{C}_6\text{H}_6/1,10\text{-phenanthroline}$ (**1**), $p\text{-MeC}_6\text{H}_4\text{Pr}'/1,10\text{-phenanthroline}$ (**2**), $\text{C}_6\text{Me}_6/1,10\text{-phenanthroline}$ (**3**), $\text{C}_6\text{Me}_6/5\text{-NO}_2\text{-1,10-phenanthroline}$ (**4**), and $\text{C}_6\text{Me}_6/5\text{-NH}_2\text{-1,10-phenanthroline}$ (**5**)) were studied by cyclic voltammetry in order to rationalize catalytic activity in transfer hydrogenation of the respective aqua complexes $[(\eta^6\text{-arene})\text{Ru}(\text{N}\cap\text{N})(\text{OH}_2)](\text{BF}_4)_2$ (**6–10**). Complexes **1–5** were chosen because the ‘true’ catalysts **6–10** are unstable under the conditions of the measurement. The electrochemical behaviour of **1–5** in acetonitrile solution is rather complicated due to consecutive and parallel chemical reactions that accompany electron transfer processes. Nonetheless, interpretation of the electrochemical data allowed to assess the influence of the structure and substitution on the redox and catalytic properties: the catalytic ability correlates with the reduction potentials, indicating the decisive role of the $\eta^6\text{-arene}$ ring directly bonded to the catalytic centre (Ru). © 2006 Elsevier B.V. All rights reserved.

Keywords: Arene complexes; Chloro complexes; Aqua complexes; Phenanthroline complexes; Ruthenium; Hydrogen transfer reduction; Cyclic voltammetry

1. Introduction

Whereas the classical coordination chemistry is typically considered as chemistry of aqueous solutions, organometallic reactions are performed almost exclusively in organic solvents due to sensitivity of many organometallic compounds towards hydrolysis. For this reason, the rigorous exclusion of water has become a general feature of laboratory techniques in this field to such an extent that water is rarely considered to be a suitable medium for reactions involving organometallic compounds. This obvious gap between organometallic and classical coordination chemis-

try is bridged by a rather narrow interface constituted by complexes containing both the soft organic and hard aqua ligands. Presumably, the first species of this type is the dinuclear cation $[(\mu\text{-O})\{(\eta^5\text{-C}_5\text{H}_5)\text{Ti}(\text{OH}_2)\}_2]^{2+}$, synthesized and isolated as the bromide salt by Wilkinson and Birmingham in 1954 and erroneously formulated as $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{OH})\text{Br}]\cdot\text{H}_2\text{O}$ [1]. The correct structure was established later spectroscopically [2] and by a single-crystal X-ray diffraction analysis [3]. The existence of arene–ruthenium aqua complexes was confirmed NMR-spectroscopically in 1972 by Zelonka and Baird in the reaction of $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ with D_2O [4]. The osmium complex cation $[(\eta^6\text{-C}_6\text{H}_6)\text{Os}(\text{OH}_2)_3]^{2+}$ was synthesised by analogy and characterized spectroscopically by Hung et al. [5]. Later, Stebler-Röthlisberger et al. succeeded in isolating the cationic complexes $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\text{OH}_2)_3]^{2+}$ and

* Corresponding authors.

E-mail addresses: stepnic@natur.cuni.cz (P. Štěpnička), georg.suess-fink@unine.ch (G. Süß-Fink).

$[(\eta^6\text{-C}_6\text{H}_6)\text{Os}(\text{OH}_2)_3]^{2+}$ as the tosylate salts and determined the structure of the triaqua(benzene)ruthenium(II) salt [6].

Since these early reports, the chemistry of organometallic aqua ions has grown steadily. This topic has been comprehensively reviewed by Koelle [7]; additional information can be found in reviews dealing with water-soluble organometallics containing hydrophilic ligands [8], metal-mediated organic synthesis in water [9], and catalysis by water-soluble organometallic complexes in biphasic systems [10]. Several recent reports deal with transfer hydrogenation of ketones with formate in aqueous media using catalytic systems based on $[(\eta^6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3\text{Pr}^i)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ and *N*-(*p*-toluenesulfonyl)-1,2-diphenyl-ethylenediamine [11–14], 2-(*N*-anilino-carboxy)pyrrolidine [15] or aminoalcohol-modified cyclodextrine [16].

While Ogo et al. reported transfer hydrogenation reactions of ketones catalysed in aqueous solution by $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{bipy})(\text{OH}_2)]^{2+}$ (bipy = 2,2'-bipyridine) [17,18], we studied two series of water-soluble cationic η^6 -arene-ruthenium complexes containing 1,10-phenanthroline or derivatives thereof as chelating *N,N*-donor ligands: $[(\eta^6\text{-arene})\text{Ru}(\text{N} \cap \text{N})\text{Cl}]\text{Cl}$ (**1–5**) and $[(\text{arene})\text{Ru}(\text{N} \cap \text{N})(\text{OH}_2)](\text{PF}_6)_2$ (**6–10**) (Scheme 1), and their catalytic potential for transfer hydrogenation of acetophenone to give 1-phenylethanol in aqueous solution using formic acid as the hydrogen source [19].

The results summarized in Fig. 1 show the observed activities to markedly differ across the series [19]. First, the catalytic activity of complexes bearing hexamethylbenzene ligand (**3–5** and **8–10**) is much higher than for their benzene or *p*-cymene analogues (**1–2** and **6–7**). Second, phenanthroline-substituted derivatives **4–5** and **9–10** exert nearly the same catalytic activity as their parent compounds **3** and **8**.

In order to rationalise the observed differences in catalytic activity, we decided to study electrochemical properties of the complexes by cyclic voltammetry. We aimed

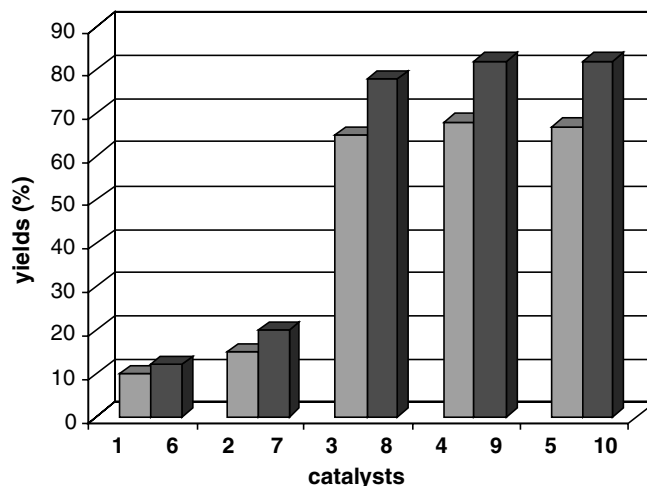


Fig. 1. Transfer hydrogenation of acetophenone to 1-phenylethanol using complexes **1–10** as catalyst precursors and HCOONa as the hydrogen donor (catalyst/acetophenone/HCOONa ratio = 1/200/6000, pH 3.8) in water (10 mL) at 50 °C for 60 h.

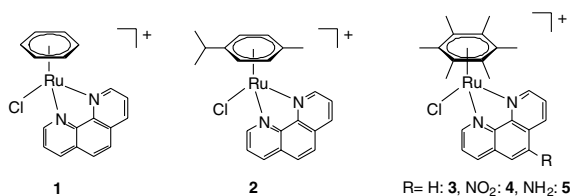
mainly at understanding of the redox properties of the above compounds in terms of localization of redox centres within the molecules, electronic interaction of different molecular parts and their influence on the redox properties. However, since the aqua complexes **6–10** are not stable under the experimental conditions,¹ we focussed on the parallel series of chloride complexes **1–5**, which are the precursors of the catalytically active solvento complexes (i.e., aqua complexes **6–10** in water).

2. Experimental

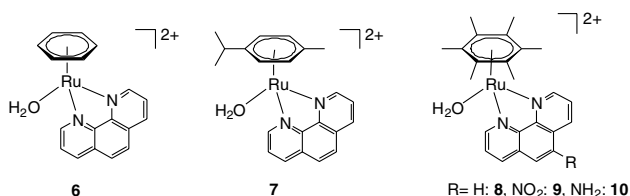
Complexes **1–5** (see Scheme 1) have been synthesised as reported previously [19]. Voltammetric measurements were performed in acetonitrile solutions containing 0.5 mM analyte and 0.1 M NBu₄PF₆ as the supporting electrolyte (Fluka, puriss. p.a.) using a computer controlled Eco-Tribo polarograph (ECO-TREND PLUS, Prague, Czech Republic) and an undivided, three-electrode system: Pt disc working electrode (diameter 0.5 mm), Ag/AgCl reference electrode separated from the analyzed solution with a non-aqueous bridge, and Pt wire as an auxiliary electrode. The measurements were performed at several scan rates (typically from 50 to 500 mV/s). The samples were deaerated with argon prior to the measurement and then kept under argon blanket. The redox potential of the ferro-

¹ Addition of solid complexes **6–10** to the base electrolyte solution (Bu₄NPF₆ in MeCN) resulted in an immediate change of the original colour of the compounds. We expect the aqua-complexes to readily undergo ligand exchange to give a solvento species. Substitution of the coordinated water molecule would be apparently facilitated by the polarity and donor ability of the solvent as well as the presence of a large molar excess of the non-coordinating base electrolyte (see also the discussion of cyclic voltammetric data in Section 3.1).

Chloro complexes **1–5**, isolated as chloride salts:



Aqua complexes **6–10**, isolated as tetrafluoroborate salts:



Scheme 1.

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