

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

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Abstract

The electrochemical properties of cationic complexes $[(\eta^6\text{-arene})\text{Ru}(\text{N} \cap \text{N})\text{Cl}]\text{Cl}$ (arene/N \cap N = C₆H₆/1,10-phenanthroline (**1**), *p*-MeC₆H₄Pr'/1,10-phenanthroline (**2**), C₆Me₆/1,10-phenanthroline (**3**), C₆Me₆/5-NO₂-1,10-phenanthroline (**4**), and C₆Me₆/5-NH₂-1,10-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 η^6 -arene ring directly bonded to the catalytic centre (Ru).

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 D₂O [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

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

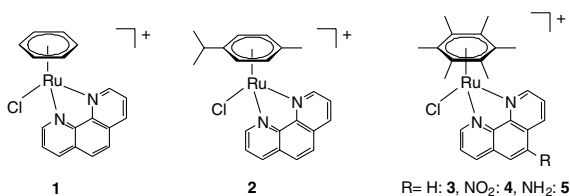
Since these early reports, the chemistry of organometallic aqua ions has grown steadily. This topic has been comprehensively reviewed by Koelle [7]; additional information can be found in reviews dealing with water-soluble organometallics containing hydrophilic ligands [8], metal-mediated organic synthesis 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 $[(\eta^6\text{-}i\text{-MeC}_6\text{H}_4\text{Pr}^i)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ and *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine [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].

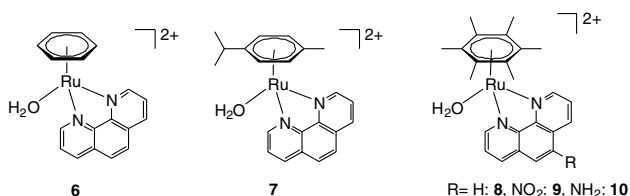
The results summarized in Fig. 1 show the observed activities to markedly differ across the series [19]. First, the catalytic activity of complexes bearing hexamethylbenzene ligand (**3–5** and **8–10**) is much higher than for their benzene or *p*-cymene analogues (**1–2** and **6–7**). Second, phenanthroline-substituted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

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



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



Scheme 1.

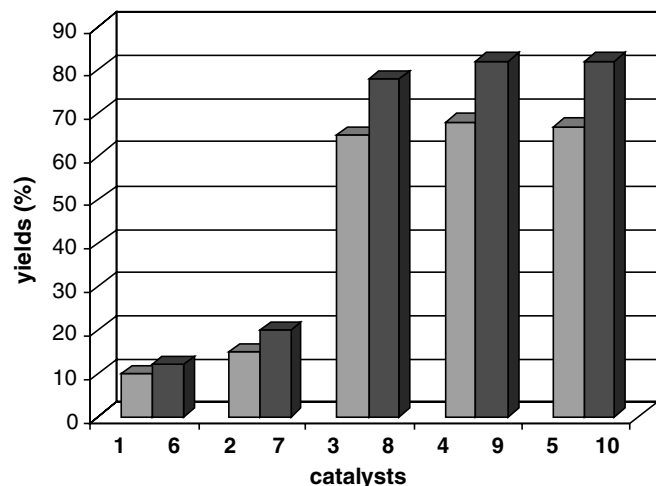


Fig. 1. Transfer hydrogenation of acetophenone to 1-phenylethanol using complexes **1–10** as catalyst precursors and HCOONa as the hydrogen donor (catalyst/acetophenone/HCOONa ratio = 1/200/6000, pH 3.8) in water (10 mL) at 50 °C for 60 h.

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 cyclovoltammetric data in Section 3.1).

cene/ferrocenium couple under the experimental conditions was 0.423 V.

3. Results and discussion

3.1. Cyclic voltammetric response and mechanistic considerations

Complexes **1–5** have been studied by cyclic voltammetry on a platinum disc electrode in acetonitrile solutions. The results obtained will be discussed along two series: the first one comprising compounds with different arene donors (**1–3**), and second, featuring different substituents in position 5 of the phenanthroline ligand (**3–5**).

The redox behaviour of complexes **1–3** is far from simple, being complicated (among other) by consecutive and parallel chemical reactions. Upon scanning towards negative potentials, all complexes (except the nitro derivative **4**; see below) undergo fast, diffusion-controlled reduction (peak I in Fig. 2). The diffusion control for this reduction was proved by linear dependence of the peak current on the concentration ($i_p \propto c$) and on the square root of the scan rate ($i_p \propto v^{1/2}$). Interestingly, this primary reduction peak has no oxidation counter-peak observable upon back scanning. Moreover, its height is approximately double than that of equimolar ferrocene as one-electron standard, indicating a two-electron reduction process.

The most probable mechanistic interpretation is as follows. The primary one-electron reduction of the parent compound (A^+) yields an unstable radical A^\cdot , which loses rapidly the chloride anion as a good “leaving group” under the formation of cation-radical B^+ . However, because the reduction potential of B^+ can be expected to be more positive as compared to A^+ , an immediate one-electron reduc-

tion occurs to give the neutral molecule **B** (standard ECE mechanism). Coordinatively unsaturated molecule **B** resulting from the loss of chloride ligand can accept one molecule of the solvent (acetonitrile or residual water) into its coordination sphere to yield a solvento (aqua) complex **C** – in its reduced form. During the reverse scan, this species is reoxidized giving rise to an anodic wave in the cyclic voltammogram (peak II). Notably, the cathodic counter-peak attributable to wave II (i.e., peak III) is only observable upon fast back-scan and its intensity increases with the scan rate (e.g., it is detectable at 0.5 V/s but not at 50 mV/s; $\Delta E_p(\text{II/III})$ for **1** is ca. 80 mV).

The formation of solvento species **C** is supported by similarity of the peak potentials for the II/III pair found for substance **1** (–0.643/–0.722 V) and the first reduction couple of the aqua complex **6** (–0.643/–0.710 V), which decomposes under the experimental conditions.¹ It is worth noting that the initial reductive loss of chloride ligand from **1–5** may be facilitated by the high polarity of the solvent and the non-coordinating electrolyte.

Comparison of cyclic voltammograms recorded at different scan rates indicates that at least two chemical reactions follow the primary electrochemical reduction: (1) the mentioned dehalogenation of the primary electrogenerated species A^\cdot which is rather fast: the height of the first two-electron peak divided by $v^{1/2}$ does not change within the range of used scan rates; and (2) relatively slow reaction(s) consuming the dehalogenated reduced complex **C** (N.B. only part of **C** can be reduced back after oxidation) under formation of a new species, which is oxidized in the next anodic step (peak IV).

Interestingly, anodic peak IV at ca. +0.5 V appears only after reductive cycling and is *not* detectable upon scanning directly into the anodic region (i.e., oxidation-only scan). Its height is much higher for **1** than for **2** and **3**. This observed difference can be explained by higher steric hindrance towards oligomerization (or aggregation) for alkylated arene derivatives (*p*-cymene and hexamethylbenzene) than for the η^6 -benzene complexes. However, the exact nature of this follow-up process remains yet unknown.

These chemical complications involve formation of products tending to bind at the electrode surface. A complete coverage of the electrode surface occurs after several cycles, resulting in a substantial change of the voltammogram. A partial reactivation of the electrode is possible by anodic polarization of the working electrode; however, full reactivation can be achieved only by mechanical polishing.

Scanning further into the region of positive potentials (even without previous reduction) revealed for all studied substances an anodic peak (V) at potentials around +1.2 V, which shifts slightly towards more positive values upon increasing the scan rate. The height and shape of this peak point to a relatively slow, irreversible (or quasi-reversible) one-electron oxidation. After reductive cycling, peak V slightly increases in height. Similarly, addition of chlorides to the analysed solution results in an increase of

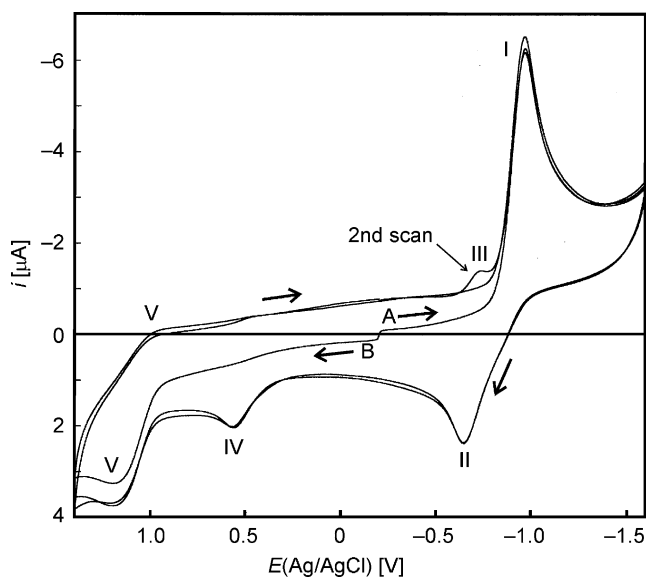


Fig. 2. Representative cyclic voltammogram of **1** as recorded on an acetonitrile solution (Pt disc electrode, 500 mV/s scan rate). Labels A and B indicate scans starting to cathodic (red/ox scan) and anodic (ox/red scan) regions, respectively.

the anodic current due to wave V, indicating an interference of this oxidation process in the parent molecule with oxidation of the liberated Cl^- ions.

As mentioned above, the overall reduction-oxidation pattern is similar for all studied molecules, except for compound **4** which exhibits the first reversible reduction wave at ca. -0.57 V attributable to one-electron reduction of the nitro group ($-\text{NO}_2 + e^- \rightleftharpoons -\text{NO}_2^{\cdot-}$). This process changes the subsequent reduction of **4** completely.

3.2. Influence of the structure

A semi-quantitative treatment of the measured potential data reflects the influence of substituents at both the η^6 -arene ring (compounds **1–3**) and the phenanthroline ligand (compounds **3–5**) upon the redox potentials (Fig. 3). For this rather simple, LFER (linear free energy relationship) approach we have used σ -*para* (σ_p) constants (-0.17 for an alkyl group, -0.66 for NH_2 and 0.78 for NO_2) [20], which seemed to be the most relevant (even if their use and additivity for η^6 -arene rings is questionable).

The data summarized in Table 1 and schematically correlated in Fig. 3 clearly show that the potentials of the first reduction (dehalogenation) process (peak I) depend *very strongly* on the arene ($190 \text{ mV}/\sigma_p$ unit in the series **1–3**). Nearly identical, strong potential dependence is observed also for the peak couple II/III, i.e. for the dehalogenated solvento (aqua) complexes, which relate closely with the true catalytically active compounds. On the other hand, the reduction potentials for wave I vary only marginally upon changing the substituent in position 5 of the phenanthroline ligand (reduction potential difference between **3** and **5** is only 15 mV , in a direction opposite to the change

Table 1
Cathodic (E_{pc}) and anodic (E_{pa}) peak potentials for waves I–V^a

| Complex | 1 | 2 | 3 | 4 | 5 | 6 |
|--------------------------|--------|--------|--------------|--------------|--------------|--------------|
| $E_{pc}(\text{I})$ [V] | -0.973 | -1.060 | -1.171 | ^b | -1.156 | -0.710 |
| $E_{pa}(\text{II})$ [V] | -0.643 | -0.656 | -0.766 | ^b | -0.794 | -0.643 |
| $E_{pc}(\text{III})$ [V] | -0.722 | -0.771 | -0.859 | ^b | -0.899 | ^d |
| $E_{pa}(\text{IV})$ [V] | 0.566 | 0.585 | ^c | ^b | ^c | ^d |
| $E_{pa}(\text{V})$ [V] | 1.183 | 1.198 | 1.180 | 1.240 | 1.140 | ^d |

^a The data were obtained at 500 mV/s and are given relative to Ag/AgCl reference.

^b The redox response is changed due to the antecedent reduction of the nitro group.

^c Data not available.

^d Further parts of the cyclic voltammogram were distorted by decomposition.

in the σ_p values). As for the potential of the oxidation peak V recorded at the same scan rate (and without any previous reductive cycling), it depends evidently on the phenanthroline ligand ($70 \text{ mV}/\sigma_p$ unit in the series **3–5**), but not on the arene ligand; the difference of the oxidation potentials is negligible in series **1–3**.

The observed variation of the redox potentials reflects intramolecular interactions between various parts of the parent complex molecules and the influence of the substituents on the redox centres present. From the above results, it is possible to conclude that whereas the reduction centre (LUMO) of the studied molecules is electronically influenced by the η^6 -coordinated arene ring, the oxidation centre (HOMO) is affected by the phenanthroline ligand and its substituents. Accordingly, the observed catalytic activity (Fig. 1) correlates only with the potential of the reduction waves (peak I and couple II/III), which indicates decisive influence of substitution at the η^6 -coordinated arene ring.

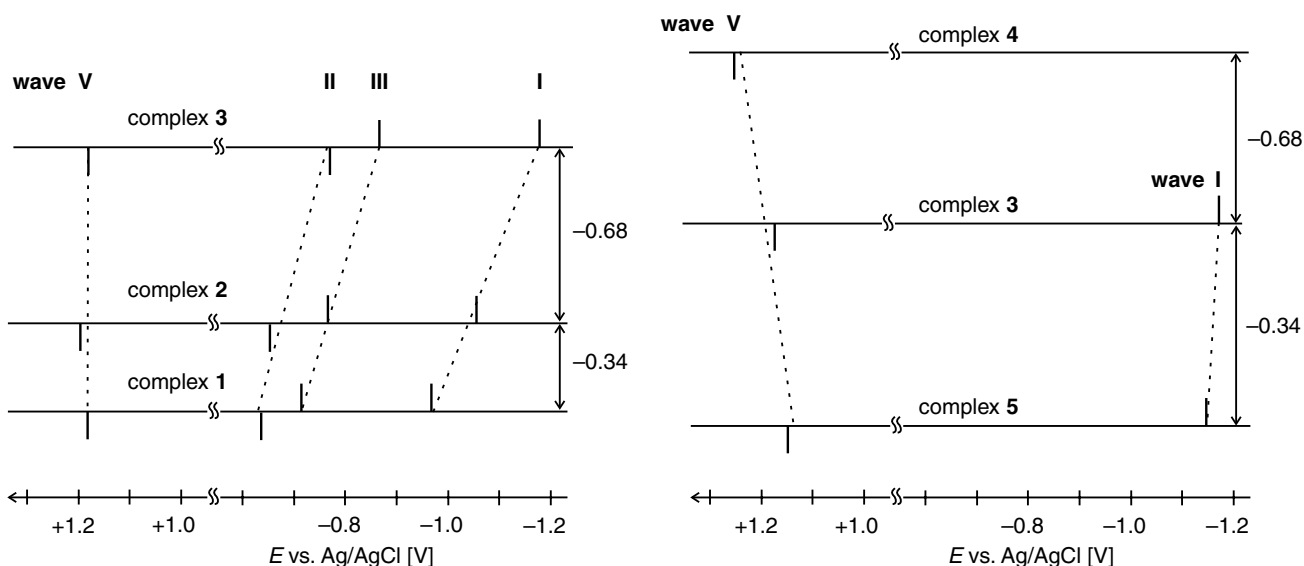
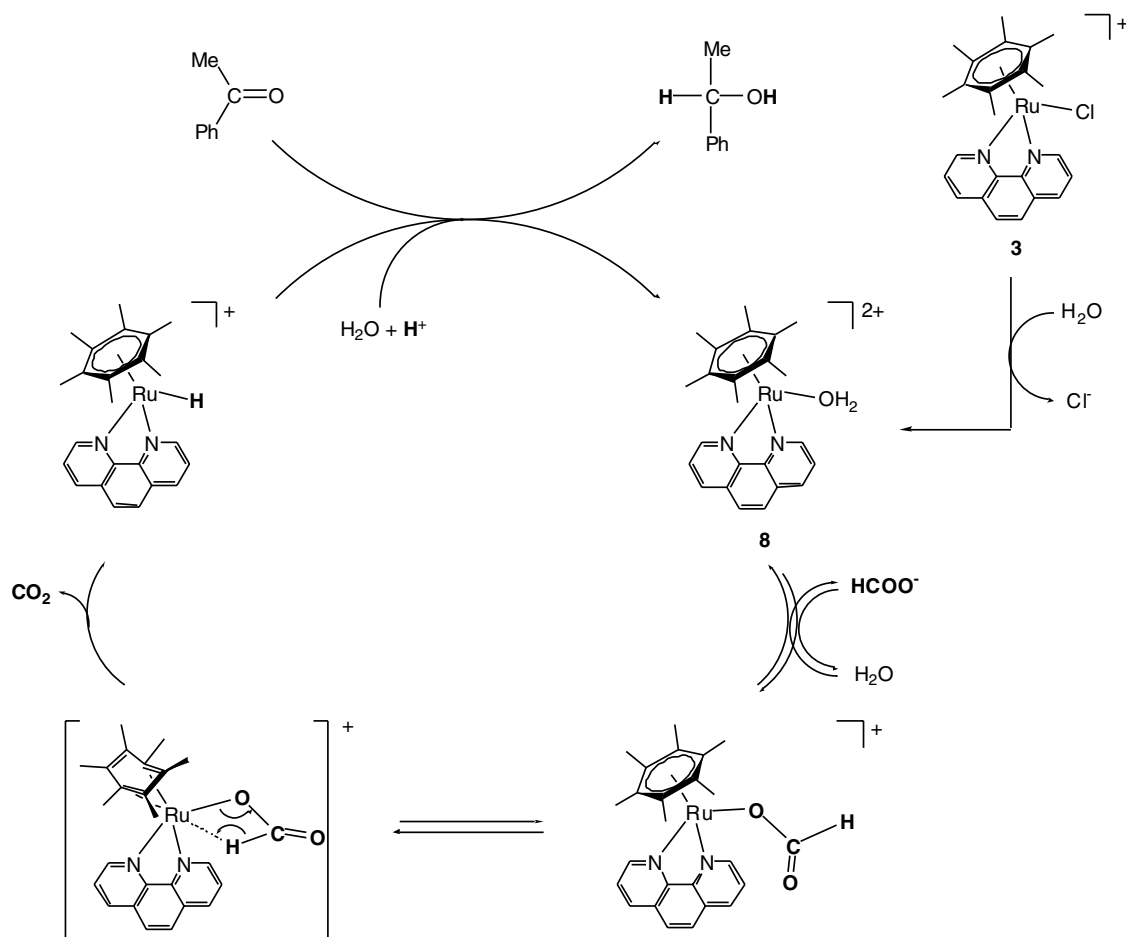


Fig. 3. Linear free energy correlations for the first (left) and second (right) series. For clarity, the positions of anodic and cathodic peaks are indicated in opposite directions with respect to the central line. Scaling in both the potential (x) and σ (y) axes is preserved for both parts of the figure to allow for a comparison of the substituent effects. Data for complex **4** are involved only partly in this correlation due to chemical complications (NO_2 group reduction; see text).



Scheme 2. Postulated catalytic cycle for the catalyst precursor **3**.

On the other hand, changing substituents in position 5 of the phenanthroline ligand (H, NO₂, NH₂) has only a negligible impact. This explains why the 1,10-phenanthroline, 5-nitro-1,10-phenanthroline and 5-amino-1,10-phenanthroline derivatives [**3** (**8**), **4** (**9**) and **5** (**10**)] exhibit very similar catalytic activities for the transfer hydrogenation despite the very different electronic properties of the substituents at the phenanthroline ligand.

The influence of the arene ligand can be rationalized on the basis of the catalytic reaction mechanism, which has been proposed [19] in view of the mechanism reported by Ogo et al. for the related bipyridine complexes [17] (Scheme 2). The most catalytically active complexes are those bearing hexamethylbenzene as the strongest electron donor (**3–5**), which accordingly exert the most negative reduction potentials for dechlorination (peak I) as well as for the successive reduction of the solvate-complex. Upon neglecting steric effects, a higher electron density at ruthenium in these complexes may influence the catalytic process by means of facilitating dissociative loss of water molecule from $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{H}_2\text{O})(\text{phen})]^+$ ions or by stabilization of electron-poor reaction intermediates, e.g., those with slipped arene ligands and $\eta^2(\text{O}^2, \text{H})$ -bonded formate.

Acknowledgements

This work was financially supported by the Swiss National Science Foundation and the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A4040304). Generous loan of ruthenium(III) chloride hydrate from the Johnson Matthey Research Centre is gratefully acknowledged.

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