

The water-soluble cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$: Improved synthesis, aerobic oxidation, electrochemical properties and ligand exchange studies

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Abstract

The synthesis of the trinuclear cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) has been considerably improved by changes in the NaBH_4 addition step and by introducing chromatographic methods; in addition, the redox and ligand exchange properties of **1** have been studied. Although exposure of an aqueous solution of **1** to air yields the oxidised cluster $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), cyclic voltammetry of $[\mathbf{1}][\text{BF}_4]$ in acetonitrile reveals a first reversible oxidation step that does not involve **2**. Bulk electrolysis of **1** and **2** in the same medium affords only decomposition products. Ligand exchange in **1** takes place only at higher temperatures: by heating a mixture of toluene with an aqueous solution of $[\mathbf{1}][\text{BF}_4]$ (1000:1) to 110 °C for 2 h, the formation of the toluene derivative $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_5\text{Me})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3**) is observed in small quantities. H/D exchange of **1** with D_2O does not occur up to 90 °C; however, in the presence of D_2 , H/D exchange with **1** is observed to give the deuterated derivative $[\text{D}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1a**). The results provide an improved synthesis of **1**, as well as information about its redox and ligand-exchange reactions, results necessary to understand and develop the chemistry of **1**.

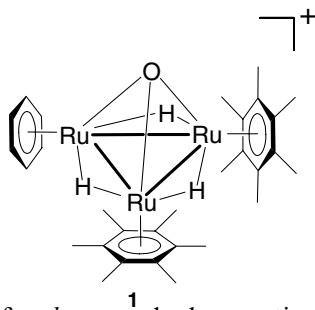
Keywords: Trinuclear clusters; Water-soluble organometallics; Arene ligands; Ruthenium

1. Introduction

In 1999, one of our groups (Süss-Fink et al.) observed that the water-soluble tetrafluoroborate salt of the trinuclear cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**), accessible from the dinuclear precursor $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$ and the mononuclear precursor $[\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$, serves as an efficient precatalyst for the hydrogenation of benzene to cyclohexane under biphasic

conditions [1]. From mass spectroscopic measurements and molecular modelling studies, and based on the observation that after the hydrogenation of C_6D_6 to give $\text{C}_6\text{D}_6\text{H}_6$ catalysed by **1**, the cluster cation could be recovered unchanged without the C_6H_6 ligand being exchanged by C_6D_6 , it was concluded that the substrate molecule is incorporated in the hydrophobic pocket spanned by the three arene ligands in **1**. This, in turn, suggested the catalytic reaction to occur within this host-guest complex without prior coordination of the substrate, a possible example of “supramolecular cluster catalysis” [2,3].

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However, for *benzene* hydrogenation catalysis derived from organometallic precatalysts the true nature of the catalytic species has remained a debatable point (“is it homogeneous or heterogeneous catalysis?”) [4]. In the case of the putative homogeneous [(C₈H₁₇)₃Me]-[RhCl₄] ion pair catalyst [5], Finke and co-workers [6] were able to demonstrate that rhodium(0) nanoclusters are the true catalysts (“soluble analogs of heterogeneous catalysts”). Benzene and other arene hydrogenation catalysts have been reviewed recently by Finke [7] and by Dyson [8], and the question of the true nature of the catalytic species in arene hydrogenation catalysis beginning with soluble metal complexes has been critically addressed by Finke et al. [9].

Prior to addressing the “is it homogeneous or heterogeneous catalysis?” question for benzene hydrogenation beginning with [1][BF₄] [9,10], it proved necessary to develop an improved synthesis for the quantities of **1** that were required, since it is difficult to obtain pure [1][BF₄] by crystallization according to the original procedure [1]. In addition, we decided to study the redox properties and the ligand exchange processes of this cluster in detail. It is these topics that are the focus of the present paper.

Elsewhere we report our collaborative kinetic studies of the benzene hydrogenation catalyzed by **1**, transmission electron microscopy studies of the reaction mixture and high-pressure in situ NMR measurements of the reaction of **1** with H₂ in D₂O, results which rule out **1** as the true catalyst. Instead, Ru(0) nanoparticles formed in small quantities from **1** under hydrogen pressure are implicated as the true catalytically active species [11]. The development of an improved synthesis of **1** was crucial to those as well as future studies of **1**, a synthesis which is reported as part of what follows.

2. Results and discussion

2.1. Improved synthesis of [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺[BF₄]⁻ (**1**)[BF₄]⁻

The well-known mononuclear triaqua complex [Ru(C₆H₆)(H₂O)₃]²⁺ [12], formed in situ from the chloro-bridged precursor [Ru(C₆H₆)Cl₂]₂ [13] in aque-

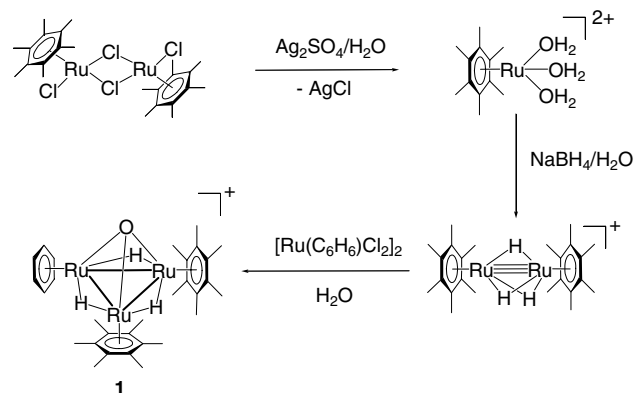
ous solution, reacts with the electron-deficient dinuclear trihydrido complex [H₃Ru₂(C₆Me₆)₂]⁺ [14] to give the trinuclear cluster cation [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺ (**1**), isolated as tetrafluoroborate salt. Herein, we report an improved synthesis and purification of [1][BF₄]⁻ based on chromatographic methods. The steps of the synthesis are summarised in Scheme 1.

Key modifications of the original procedure are: (i) the slow (dropwise) addition of the aqueous NaBH₄ solution via an oxygen-free cannula with cooling to 10 °C in order to avoid foaming; and (ii) purification of the [1][BF₄]⁻ precipitate by preparative thin-layer chromatography on silica-gel using a dichloromethane–acetone mixture (2:1) as eluant to remove NaBF₄, by-products and other contaminants. The details are given in Section 4.

2.2. Aerobic oxidation of [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺ (**1**) to [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)(OH)]⁺ (**2**)

Exposure of an aqueous solution of [1][BF₄]⁻ to air gives the oxidised cluster [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)(OH)]⁺ (**2**), although **1** is not noticeably air-sensitive in its solid form. This reaction is best carried out in aqueous solution under atmospheric pressure of air, the complete conversion of **1** into **2** taking about 4 days. An NMR study of the conversion of **1** into **2**, carried out at 27 °C in D₂O solution with approximately 10 equivalents of O₂ (with respect to **1**), shows no indication of any detectable intermediary species. On the other hand, under hydrogen pressure (60 bars) at 110 °C, **2** converts back quantitatively into **1** within 2 h (see Fig. 1).

The reversible transformation of **1** into **2** in aqueous solution suggests interesting redox properties of these clusters. Hence, these were studied by electrochemical methods as detailed in the next section.



Scheme 1.

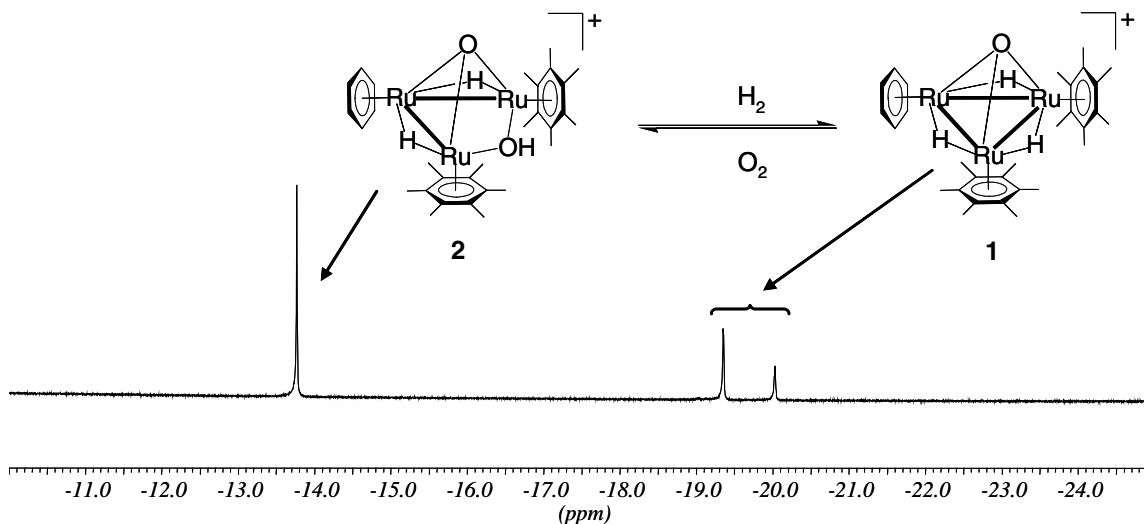


Fig. 1. Conversion of **2** into **1** with molecular hydrogen and the conversion of **1** back into **2** with 0.5 equivalent of molecular oxygen. The ^1H NMR spectrum shows a D_2O solution of both **1** and **2**. (The enlargement reveals the hydride signal of **2** being a singlet at $\delta = -13.77$ ppm, while the hydride signals of **1** show the expected multiplicities [$\delta = -19.35$ ppm (doublet) and $\delta = -20.03$ ppm (triplet)] in a 2:1 integral ratio).

2.3. Electrochemical properties of $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) and $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**)

Cyclic voltammetry (scan rate 0.1 V s^{-1}) of **1** (Fig. 2) in a deoxygenated solution of acetonitrile shows, in the potential range 0 to $+1.5 \text{ V}$ versus SCE, three successive anodic peaks ($E_{\text{pa}_1} = +0.52 \text{ V}$ versus SCE; $E_{\text{pa}_2} = +0.90 \text{ V}$ versus SCE; $E_{\text{pa}_3} = +1.29 \text{ V}$ versus SCE). Only the first one corresponds to a chemically and electrochemically reversible system ($E_{\text{pa}_1} = +0.52 \text{ V}$ versus SCE; $E_{\text{pc}_1} = +0.45 \text{ V}$ versus SCE). The same behaviour was observed at a glassy carbon or a platinum electrode

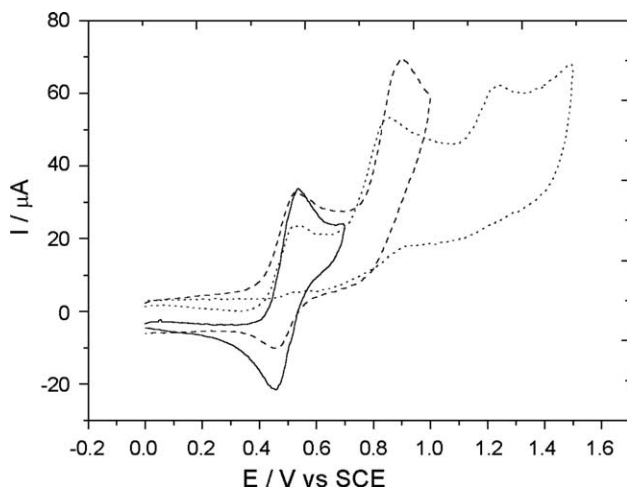


Fig. 2. Cyclic voltammetry of a saturated solution of $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$ in acetonitrile $+0.1 \text{ M Bu}_4\text{NClO}_4$ at a glassy carbon electrode, by varying the potential from 0 V_{SCE} to $0.7 \text{ V}_{\text{SCE}}$ (—), 1 V_{SCE} (----) and $1.5 \text{ V}_{\text{SCE}}$ (···). Scan rate: 0.1 V s^{-1} .

using either 0.1 M LiClO_4 or $0.1 \text{ M Bu}_4\text{NClO}_4$ containing H_2O (10%), as electrolyte.

Complex **2** in acetonitrile is irreversibly oxidised at a potential ($+0.46 \text{ V}$ versus SCE) close to **1** (Fig. 3). Consequently, the anodic oxidation of **1** cannot give **2** as final product. Other ill-defined irreversible waves are observed at higher potential. Moreover, **1** and **2** are not reduced in the potential range 0 to -2 V versus SCE.

Bulk electrolysis at a working potential corresponding to the plateau of the first anodic wave ($+0.6 \text{ V}$ versus SCE) of **1** and **2** in deoxygenated acetonitrile both involve about 2–3 F per mol. Electrolysis of **1** was monitored by voltammetry at a platinum rotating disc

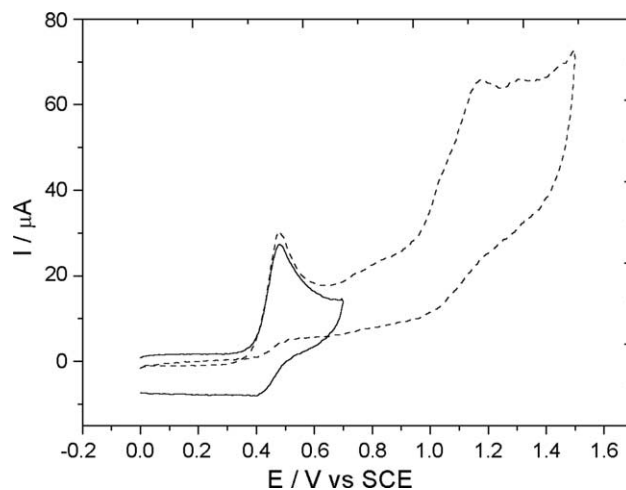


Fig. 3. Cyclic voltammetry of a saturated solution of $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})][\text{BF}_4]$ ($3 \times 10^{-3} \text{ mol L}^{-1}$) in acetonitrile $+0.1 \text{ M Bu}_4\text{NClO}_4$ at a glassy carbon electrode, by varying the potential from 0 V_{SCE} to $0.7 \text{ V}_{\text{SCE}}$ (—) and $1.5 \text{ V}_{\text{SCE}}$ (----). Scan rate: 0.1 V s^{-1} .

electrode. The first anodic wave ($E_{1/2} = +0.48$ V versus SCE) decreased during electrolysis without the appearance of the expected reversible cathodic wave observed by cyclic voltammetry of **1**. A transient cathodic wave ($E_{1/2} = -0.03$ V versus SCE) which totally disappeared at the end of electrolysis was observed.

Thus, under the time scale of a macroscale electrolysis, the product resulting from the anodic oxidation of **1** is not stable enough to be isolated. After work up, $[(C_6Me_6)_2Ru_2(OH)_3]^+$ was identified from the mixture of decomposition products. After electrolysis of **2**, $[(C_6Me_6)_2Ru_2(OH)_3]^+$ was also identified from the mixture of isolated products by electrospray mass spectrometry of the acetone extract.

In summary, the redox behaviour of **1** and **2** is more complicated than it appears from the reversible aerobic oxidation of **1–2** in aqueous solution: under electrochemical conditions and in the absence of H^+ , **1** and **2** surprisingly do not interconvert.

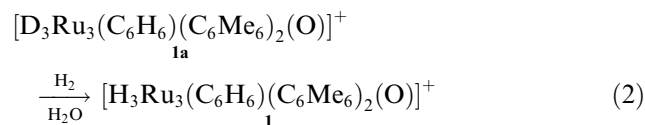
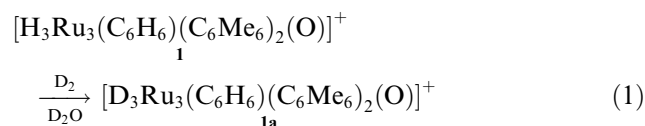
2.4. Ligand exchange studies

The catalytic activity of **1** for the hydrogenation of arenes evokes the question whether or not the arene and/or hydrido ligands in **1** are involved in the catalytic process. This is why we studied ligand exchange reactions of **1** with arenes, with molecular hydrogen and with water.

Previously we observed that the hydrogenation of hexadeutero-benzene, C_6D_6 , catalysed by $[H_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1**) under biphasic conditions (catalyst/substrate ratio 1:1000, 110 °C, 60 bar) yields the expected 1,2,3,4,5,6-hexadeuterocyclohexane, while cluster **1** still contains one C_6H_6 and two C_6Me_6 ligands (and no coordinated C_6D_6) after the catalytic reaction, according to NMR and MS data [15]. It was of interest, therefore, to study the exchange reactions of **1** with other arenes: in the case of toluene hydrogenation (catalyst/substrate ratio 1:1000, 110 °C, 60 bar), exchange of the benzene ligand for a toluene molecule is indeed

observed. While the 1H NMR spectrum of the organometallic residue of the aqueous phase dissolved in D_2O showed only the expected signals of **1**, the electrospray mass spectrum of the organometallic residue revealed a small amount of the toluene-exchanged cluster $[H_3Ru_3(C_6H_5Me)(C_6Me_6)_2(O)]^+$ (**3**). Given that this cluster is not visible in the NMR spectrum, we estimate its presence to less than 5%. The same exchange (less than 5%) takes place by heating a mixture of toluene with an aqueous solution of **1** (1000:1) for 2 h to 110 °C without hydrogen pressure. However, in all cases the extent of the arene exchange in **1** is <5%.

High-pressure in situ NMR measurements of the reaction of **1** with D_2 in D_2O and of the deuterated derivative $[D_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ (**1a**) with H_2 in H_2O were performed in order to study the possible H/D and D/H exchange reactions affecting hydrido and deuterido ligands, respectively (Eqs. (1) and (2)).



Under a pressure of 50 bar of D_2 (or H_2 , respectively) we observed complete H/D exchange according to Eqs. (1) and (2) at 90 °C over a period of 6 h (Fig. 4). The exchange reaction does not take place at temperatures below 80 °C, however. As shown in Fig. 4, partially deuterated derivatives $[H_2DRu_3(C_6H_6)(C_6Me_6)_2(O)]^+$ and $[HD_2Ru_3(C_6H_6)(C_6Me_6)_2(O)]^+$ are not observed, at least not in concentrations detectable by NMR.

Hydrogen (or deuterium) pressure is required for the H/D exchange process: an NMR study of **1** in D_2O without D_2 (or **1a** in H_2O without H_2) reveals that the hydride signals of the cluster remain unchanged even

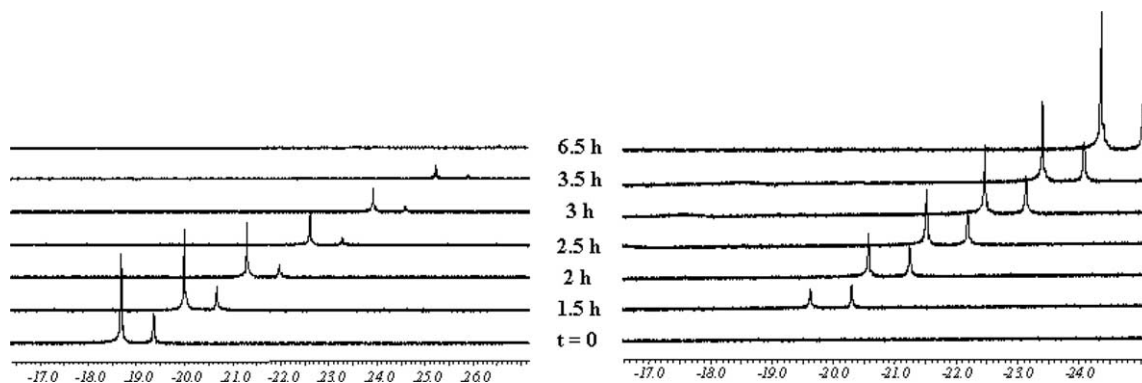


Fig. 4. NMR spectra showing H/D exchange reaction affecting hydrido ligands in **1** (on the left) and D/H exchange reaction affecting deuterido ligands in **1a** at 90 °C under 50 bar of D_2 in D_2O and 50 bar of H_2 in H_2O , respectively.

at 90 °C over a period of 24 h. That is, there is no exchange of the hydrido ligands in **1** with water even at 90 °C.

3. Summary

In conclusion, an improved preparation resulting in 51% of pure $[\mathbf{1}][\text{BF}_4]$ (185 mg scale) has been reported. We have also surveyed the electrochemistry and H/D and arene exchange reactions of $[\mathbf{1}][\text{BF}_4]$. The results show that while $[\mathbf{1}][\text{BF}_4]$ is a novel composition and structure organometallic complex, it is quite stable and relatively unreactive. These findings are consistent with our conclusions elsewhere that trace $\text{Ru}(0)_n$ nanoclusters are the true benzene hydrogenation catalyst derived from $[\mathbf{1}][\text{BF}_4]$ and not this otherwise interesting organometallic complex itself.

4. Experimental

4.1. Syntheses

General remarks: All manipulations were carried out in an inert argon atmosphere using standard Schlenk techniques unless stated otherwise. Filtrations were carried out using a Mülheim apparatus. Doubly distilled water was degassed and saturated with argon prior to use. Organic solvents used for chromatography were distilled under argon prior to use. Silica-gel G used for preparative thin-layer (20 × 20 cm) chromatography was purchased from Macherey-Nagel GmbH. NMR spectra were recorded using a Bruker 400 MHz spectrometer. Electrospray mass spectra were obtained in positive-ion mode using a LCQ Finnigan mass spectrometer. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. The starting dinuclear complexes $[\text{Ru}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2$ [16] and $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ [13] were prepared according to published methods.

4.1.1. Improved preparation of $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$ ($[\mathbf{1}][\text{BF}_4]$)

In a 250 mL brown-glass Schlenk tube, 300 mg (0.449 mmol) of $[\text{Ru}(\text{C}_6\text{Me}_6)\text{Cl}_2]_2$ were mixed with a solution of 282 mg (0.904 mmol) of Ag_2SO_4 in 30 mL of water. The suspension was stirred at room temperature until the orange solid has completely dissolved to give a yellow solution of $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{H}_2\text{O})_3]^{2+}$ (around one hour). The white precipitate of AgCl formed was removed from the aqueous solution by filtration through filter pulp. The resulting clear yellow filtrate was cooled in an ice-bath for 30 min. In a separate 50 mL Schlenk tube, 75 mg (1.974 mmol) of NaBH_4 were dissolved in 15 mL of water at room temperature. After stirring for

5 min, the NaBH_4 solution was transferred very slowly through a cannula into the ice-bath-cooled $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{H}_2\text{O})_3][\text{SO}_4]$ solution. The colour of the solution changed to black, due to the formation of $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$. The resulting solution was immediately filtered through filter pulp under argon to remove insoluble black particles. To the dark solution containing $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$, solid $[\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2$ (210 mg, 0.420 mmol) was added. The mixture was stirred at room temperature, until the orange solid had completely dissolved. Then, the solution was transferred under argon into a 300 mL closed Schlenk pressure tube and stirred under argon pressure (two atmospheres) at 60 °C for 3 days.

During this time, the colour of the solution changed from black to red. After cooling to room temperature, the red solution containing **1** was filtered through filter pulp. Then a large excess of solid NaBF_4 was added to the filtrate to precipitate $[\mathbf{1}][\text{BF}_4]$. After stirring for one hour at room temperature, the red precipitate was centrifuged in air (1500 rpm, 10 min), the aqueous solution was removed from the centrifuge tube with a glass pipette. The red solid was dissolved in CH_2Cl_2 and again filtered through filter pulp to eliminate excess NaBF_4 . Then the methylene chloride solution was concentrated to 15 mL in vacuo. The resulting solution was subjected to preparative thin-layer chromatography on silica-gel using $\text{CH}_2\text{Cl}_2/\text{acetone}$ (2/1) as eluant. The pure $[\mathbf{1}][\text{BF}_4]$ was extracted from the main red band with acetone. Evaporation of acetone under vacuum gave 185 mg (51%) of $[\mathbf{1}][\text{BF}_4]$ as a red powder.

Spectroscopic data for **1**: ^1H NMR (400 MHz, acetone- d_6): $\delta = -19.93$ (t, 1H, $^2J = 3.84$ Hz, Ru-H), -19.08 (d, 2H, $^2J = 3.84$ Hz, Ru-H), 2.31 (s, 36H, $\text{C}_6(\text{CH}_3)_6$), 5.70 (s, 6H, C_6H_6). $^{13}\text{C}\{^1\text{H}\}$ (50 MHz, acetone- d_6): $\delta = 17.48, 71.45, 95.06$. MS (ESI positive mode, in acetone): m/z : 726 $[\text{M} + 2\text{H}]^+$.

4.1.2. Preparation of $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$ ($[\mathbf{2}][\text{BF}_4]$)

In a Schlenk pressure tube, a red solution of 50 mg (0.062 mmol) of $[\mathbf{1}][\text{BF}_4]$ in 80 mL of water were heated at 50 °C under about 3 bars of air during 3 days. The resulting orange-yellow solution was filtered through filter pulp, and then the water was removed by evaporation under reduced pressure. The residue was dissolved in 5 mL of CH_2Cl_2 and subjected to preparative thin-layer chromatography on silica-gel using $\text{CH}_2\text{Cl}_2/\text{acetone}$ (2/1) as eluant. The pure $[\mathbf{2}][\text{BF}_4]$ was extracted from the main orange band with acetone. Evaporation of acetone under vacuum gave 20 mg (39%) of $[\mathbf{2}][\text{BF}_4]$ as an orange powder.

Spectroscopic data for **2**: ^1H NMR (400 MHz, acetone- d_6): $\delta = -13.67$ (s, 2H, Ru-H), 2.15 (s, 36H, $\text{C}_6(\text{CH}_3)_6$), 5.82 (s, 6H, C_6H_6). MS (ESI positive mode, in acetone): m/z : 742 $[\text{M} + \text{H}]^+$.

4.1.3. Preparation of $[D_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]\text{-}[BF_4]$ ($[1a][BF_4]$)

The deuterated derivative $[1a][BF_4]$ was prepared and purified according to the same procedure as $[1][BF_4]$, water being replaced by heavy water and $NaBH_4$ being replaced by $NaBD_4$. However, the yield is significantly lower (less than 20%).

Spectroscopic data for **1a**: 1H NMR (400 MHz, acetone- d_6): δ = 2.31 (s, 36H, $C_6(CH_3)_6$), 5.70 (s, 6H, C_6H_6). $^{13}C\{^1H\}$ (50 MHz, acetone- d_6): δ = 17.48, 71.45, 95.06. MS (ESI positive mode, in acetone): m/z : 728 $[M + H]^+$.

4.2. Electrochemical studies

Conventional electrochemical equipment was used for cyclic voltammetry and voltammetry at a rotating disc electrode (EG&G Princeton applied Research Model 362 scanning potentiostat with an XY recorder or a power Lab/4SP, Scope version 3.6.10, ADInstrument). For both cyclic voltammetry or voltammetry at a rotating disc electrode (ω = 2000 rpm), the working electrode was a disc of glassy carbon (3 mm diameter) or platinum (1 mm diameter). All potentials referred to the saturated calomel electrode (SCE) and were not corrected for the ohmic drop. The $E_{1/2}$ and ΔE_p of ferrocene in our cell were + 0.40 V versus SCE and 0.08 V versus SCE, respectively.

Controlled potential electrolyses were performed in a divided cell [17] equipped with a planar platinum electrode (4 cm diameter). The coulometric measurements were determined with a current integrator Tacussel IG5. Electrolyses under continuous bubbling of nitrogen generally involve 3×10^{-5} – 8×10^{-5} mol of substance **1** or **2** in 50 mL of non-dried CH_3CN containing 0.2 M $LiClO_4$ as electrolyte. After electrolysis of **1** and **2**, water (50 mL) was added to the electrolysed solution. Acetonitrile was removed in vacuo before adding an aqueous solution of HBF_4 . The resulting solution was extracted twice with CH_2Cl_2 which was dried over magnesium sulfate and evaporated in vacuo. The resultant red solid was washed with diethyl ether.

4.3. Ligand exchange studies

4.3.1. Arene exchange study

In a 300 mL closed Schlenk pressure tube was stirred a mixture of an aqueous solution of $[1][BF_4]$ (10 mg, 1.23×10^{-5} mol, 10 mL) with toluene (1.32 mL, 12.3 mmol) for 2 h at 110 °C. After cooling, the toluene was removed by decanting and extraction with 5 mL of diethyl ether followed by evaporation of the aqueous solution to dryness under reduce pressure. The red residue was analysed by 1H NMR spectroscopy and by mass spectrometry.

4.3.2. Hydride exchange studies (high-pressure NMR experiments)

All H–D or D–H exchange experiments were carried out under oxygen-free conditions using glove box and Schlenk techniques. D_2O (99.9%) was purchased from Cambridge Isotope Laboratories, whereas D_2 was purchased from Linde. Experiments under pressure were carried out in a 10 mm medium pressure sapphire NMR-tube [18] under 5 MPa of H_2 or D_2 pressure. Spectra were collected on a Bruker DRX 400 MHz instrument, the integrals were calculated using the WIN-NMR program and the 1H chemical shifts were referenced to 3-trimethylsilyl-1-propanesulfonic acid Na salt (TSPSANA), external standard.

The exchange reactions were carried out at 363 K temperature, using **1a** or **1** under 50 bars of H_2 or D_2 pressure in solvent H_2O or D_2O , respectively. The time delays between spectra are 10 min in case of D–H exchange and 20 min in case of H–D exchange. In case of D–H exchange, the measurements were carried out in sweep off mode and use a water suppression pulse sequence (1-3-3-1) because of lack of lock and the presence of the large H_2O signal [19].

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