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 NaBH₄ 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 [1][BF₄] 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 [1][BF₄] (1000:1) to 110 °C for 2 h, the formation of the toluene derivative \([\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+\) (3) is observed in small quantities. H/D exchange of 1 with D₂O does not occur up to 90 °C; however, in the presence of D₂, 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 \([\text{H}_2\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+\) 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 \(\text{C}_6\text{D}_6\) to give \(\text{C}_6\text{D}_6\text{H}_6\) catalysed by 1, the cluster cation could be recovered unchanged without the \(\text{C}_6\text{H}_6\) ligand being exchanged by \(\text{C}_6\text{D}_6\), 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].
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 \([\text{[C}_6\text{H}_6\text{]}_2\text{Me}][\text{RhCl}_3]\) 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 \([\text{[BF}_4]\) [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 \([\text{[BF}_4]\) 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 \(\text{H}_2\) in \(\text{D}_2\text{O}\), 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 \([\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]\) (1) and \([\text{[BF}_4]\) \([\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]\)

The well-known mononuclear triaqua complex \([\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}\) [12], formed in situ from the chloro-bridged precursor \([\text{Ru}(\text{C}_6\text{H}_6)\text{Cl}_2]_2\) [13] in aqueous solution, reacts with the electron-deficient dinuclear trihydrido complex \([\text{H}_3\text{Ru}_3(\text{C}_6\text{Me}_6)_2]^{14}\) to give the trinuclear cluster cation \([\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]\) (1), isolated as tetrafluoroborate salt. Herein, we report an improved synthesis and purification of \([\text{[BF}_4]\) 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 NaBF4 solution via an oxygen-free cannula with cooling to 10 °C in order to avoid foaming; and (ii) purification of the \([\text{[BF}_4]\) 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 \([\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]\) (1) to \([\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})][\text{BF}_4]\) (2)

Exposure of an aqueous solution of \([\text{[BF}_4]\) to air gives the oxidised cluster \([\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})][\text{BF}_4]\) (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 \(\text{D}_2\text{O}\) solution with approximately 10 equivalents of \(\text{O}_2\) (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.
2.3. Electrochemical properties of [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺ (1) and [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)-(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 V versus SCE, three successive anodic peaks (Eₚa₁ = +0.52 V versus SCE; Eₚa₂ = +0.90 V versus SCE; Eₚa₃ = +1.29 V versus SCE). Only the first one corresponds to a chemically and electrochemically reversible system (Eₚa₁ = +0.52 V versus SCE; Eᵣᵣ₁ = +0.45 V versus SCE). The same behaviour was observed at a glassy carbon or a platinum electrode using either 0.1 M LiClO₄ or 0.1 M BuNCIO₄ containing H₂O (10%), as electrolyte.

Complex 2 in acetonitrile is irreversibly oxidised at a potential (+0.46 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 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.

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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 $^1$H NMR spectrum shows a D₂O solution of both 1 and 2. (The enlargement reveals the hydride signal of 2 being a singlet at δ = −13.77 ppm, while the hydride signals of 1 show the expected multiplicities [δ = −19.35 ppm (doublet) and δ = −20.03 ppm (triplet)] in a 2:1 integral ratio).

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Fig. 2. Cyclic voltammetry of a saturated solution of [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)][BF₄] in acetonitrile +0.1 M Bu₄NClO₄ at a glassy carbon electrode, by varying the potential from 0 Vₛₑᶜₑ to 0.7 Vₛₑᶜₑ (——), 1 Vₛₑᶜₑ (-----) and 1.5 Vₛₑᶜₑ (····). Scan rate: 0.1 V s⁻¹.

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Fig. 3. Cyclic voltammetry of a saturated solution of [H₂Ru₃(C₆H₆)(C₆Me₆)₂(O)(OH)][BF₄] (3 × 10⁻⁸ mol L⁻¹) in acetonitrile +0.1 M Bu₄NClO₄ at a glassy carbon electrode, by varying the potential from 0 Vₛₑᶜₑ to 0.7 Vₛₑᶜₑ (——) and 1.5 Vₛₑᶜₑ (-----). Scan rate: 0.1 V s⁻¹.
electrode. The first anodic wave \( (E_{1/2} = \pm 0.48 \text{ V versus SCE}) \) decreased during electrolysis without the appearance of the expected reversible cathodic wave observed by cyclic voltammetry of 1. A transient cathodic wave \( (E_{1/2} = -0.03 \text{ V versus SCE}) \) 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, \([\text{C}_6\text{Me}_6]_2\text{Ru}_3(\text{OH}_3^+)\] was identified from the mixture of decomposition products. After electrolysis of 2, \([(\text{C}_6\text{Me}_6)_2\text{Ru}_2(\text{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 \( \text{H}^+ \), 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 hexadeuterobenzene, \( \text{C}_6\text{D}_6 \), catalysed by \( [\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{OH})]\) (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 \( \text{C}_6\text{H}_6 \) and two \( \text{C}_6\text{Me}_6 \) ligands (and no coordinated \( \text{C}_6\text{D}_6 \)) 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 \( ^1\text{H} \) NMR spectrum of the organometallic residue of the aqueous phase dissolved in \( \text{D}_2\text{O} \) showed only the expected signals of 1, the electrospray mass spectrum of the organometallic residue revealed a small amount of the toluene-exchanged cluster \( [\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_5\text{Me})(\text{C}_6\text{Me}_6)_2(\text{O})]^{+} \) (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 \( \text{D}_2 \) in \( \text{D}_2\text{O} \) and of the deuterated derivative \( [\text{D}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^{+} (1\text{a}) \) with \( \text{D}_2 \) in \( \text{H}_2\text{O} \) 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)).

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\begin{align*}
[H_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ & \\
\frac{D_2}{D_2} & [D_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ (1) \\
[D_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ & \\
\frac{[D_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ (1a)}{H_2} & [H_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ (2)
\end{align*}
\]

Under a pressure of 50 bar of \( \text{D}_2 \) (or \( \text{H}_2 \), 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 \( [\text{H}_2\text{D}\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ \) and \( [\text{HD}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+ \) are not observed, at least not in concentrations detectable by NMR.

![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 D2 in D2O and 50 bar of H2 in H2O, respectively.](image-url)
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 [1][BF₄] (185 mg scale) has been reported. We have also surveyed the electrochemistry and H/D and arené exchange reactions of [1][BF₄]. The results show that while [1][BF₄] 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 Ru(0), nanoclusters are the true benzene hydrogenation catalyst derived from [1][BF₄] 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 x 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 [Ru(C₆Me₆)Cl₂] [16] and [Ru(C₆H₅)-Cl₂] [13] were prepared according to published methods.

4.1.1. Improved preparation of [H₂Ru₂(C₆H₅)(C₆Me₆)₂(η²-η¹)] (1)[BF₄] (1)[BF₄]

In a 250 mL brown-glass Schlenk tube, 300 mg (0.449 mmol) of [Ru(C₆Me₆)Cl₂] were mixed with a solution of 282 mg (0.904 mmol) of Ag₂SO₄ 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 [Ru(C₆Me₆)(H₂O)]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 NaBH₄ were dissolved in 15 mL of water at room temperature. After stirring for 5 min, the NaBH₄ solution was transferred very slowly through a cannula into the ice-bath-cooled [Ru(C₆-Me₆)(H₂O)]²⁺[SO₄] solution. The colour of the solution changed to black, due to the formation of [H₂Ru₂(C₆Me₆)₂]²⁻. The resulting solution was immediately filtered through filter pulp under argon to remove unsoluble black particles. To the dark solution containing [H₂Ru₂(C₆Me₆)₂]²⁻, solid [Ru(C₆H₅)Cl₂] (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 NaBF₄ was added to the filtrate to precipitate [1][BF₄]. 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 CH₂Cl₂ and again filtered through filter pulp to eliminate excess NaBF₄. 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 CH₂Cl₂/acetone (2/1) as eluant. The pure [1][BF₄] was extracted from the main red band with acetone. Evaporation of acetone under vacuum gave 185 mg (51%) of [1][BF₄] as a red powder.

Spectroscopic data for 1: ¹H NMR (400 MHz, acetone-d₆): δ = −19.93 (t, 1H, J = 3.84 Hz, Ru(η²)), −19.08 (d, 2H, J = 3.84 Hz, Ru(η¹)), 2.31 (s, 36H, C₆(CH₃)₃), 5.70 (s, 6H, C₆H₆). ¹³C [¹H] (50 MHz, acetone-d₆): δ = 17.48, 71.45, 95.06 MS (ESI positive mode, in acetone): m/z: 726 [M + 2H]⁺.

4.1.2. Preparation of [H₂Ru₃(C₆H₅)(C₆Me₆)₂(η²-η¹)(OH)] [BF₄] (1)[BF₄]

In a Schlenk pressure tube, a red solution of 50 mg (0.062 mmol) of [1][BF₄] 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 CH₂Cl₂ and subjected to preparative thin-layer chromatography on silica-gel using CH₂Cl₂/acetone (2/1) as eluant. The pure [2][BF₄] was extracted from the main orange band with acetone. Evaporation of acetone under vacuum gave 20 mg (39%) of [2][BF₄] as an orange powder.

Spectroscopic data for 2: ¹H NMR (400 MHz, acetone-d₆): δ = −13.67 (s, 2H, Ru(η²)), 2.15 (s, 36H, C₆(CH₃)₃), 5.82 (s, 6H, C₆H₆). MS (ESI positive mode, in acetone): m/z: 742 [M + H]⁺.
4.1.3. Preparation of $[D_3Ru_3(C_6H_6)(C_6Me_6)_2(O)]$-$[BF_4]$ (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$_6$): $\delta = 2.31$ (s, 36H, C$_6$(CH$_3$)$_3$), 5.70 (s, 6H, C$_6$H$_6$). $^{13}$C$[^1H]$ (50 MHz, acetone-d$_6$): $\delta = 17.48$, 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, ADInstruments). For both cyclic voltammetry or voltammetry at a rotating disc electrode ($\omega = 2000$ 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 $\Delta E_p$ of ferrocene in our cell were $\pm 0.40$ 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 $3 \times 10^{-5}$ – $8 \times 10^{-5}$ mol of substance 1 or 2 in 50 mL of non-dried CH$_3$CN 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$_3$Cl$_2$ 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 $[1a][BF_4]$ (10 mg, 1.23 $\times 10^{-5}$ 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$_2$O (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 (TSPSNa), external standard.

The exchange reactions were carried out at 363 K temperature, using 1a or I under 50 bars of H$_2$ or D$_2$ pressure in solvent H$_2$O or D$_2$O, 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$_2$O signal [19].

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