

endo and *exo* Coordination of Indanol: Synthesis, Isolation and Structural Characterisation of $[\text{H}_3\text{Ru}_3(\textit{endo}\text{-Indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ and $[\text{H}_3\text{Ru}_3(\textit{exo}\text{-Indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ as Their Tetrafluoroborate Salts

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The reaction of 2,3,4,7-tetrahydro-1*H*-inden-2-ol with ruthenium chloride hydrate in refluxing ethanol yields the chloro-bridged dinuclear complex $[\text{RuCl}_2(\textit{indanol})]_2$ (**1**). The mononuclear complex $[\text{Ru}(\textit{indanol})(\text{H}_2\text{O})_3]^{2+}$ (**2**), formed in situ from **1** in aqueous solution, reacts with the dinuclear complex $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$ to give a trinuclear arene-ruthenium cluster as a mixture of two isomers, the cations $[\text{H}_3\text{Ru}_3(\textit{endo}\text{-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3a**) and $[\text{H}_3\text{Ru}_3(\textit{exo}\text{-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3b**), in a 1:1 ratio. The hydroxy function of the indanol ligand is oriented towards the μ_3 -oxo cap of **3a**, whereas the OH group is bent away from the metal skeleton of **3b**. These two isomers, which can easily be separated by silica-gel chromatography, were isolated and characterised

as their tetrafluoroborate salts. The single-crystal X-ray structure analysis of $[\mathbf{3a}][\text{BF}_4]$ shows a strong intramolecular hydrogen bond between the μ_3 -oxo ligand and the hydroxyl function, which even persists in acetone solution, as demonstrated by NMR spectroscopy. On the other hand, the hydroxy function of **3b** was found to be free in the solid state as well as in solution, as shown by an X-ray crystal structure analysis and by NMR spectroscopy. The catalytic activities of the water-soluble trinuclear cations **3a** and **3b** for the hydrogenation of benzene to give cyclohexane under biphasic conditions are considerably different, the *exo* isomer **3b** being more active than the *endo* isomer **3a**.

Introduction

We reported recently that the cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$, used as its water-soluble tetrafluoroborate salt, efficiently catalyses the hydrogenation of benzene to cyclohexane under biphasic conditions.^[1] From experimental and molecular modelling studies we concluded that the substrate molecule is incorporated into the hydrophobic pocket spanned by the three arene ligands, suggesting that the catalytic reaction occurs within this host-guest complex without prior coordination of the substrate ("supramolecular cluster catalysis").^[2] Furthermore, we were able to isolate the catalyst-substrate host-guest complexes postulated for two hydroxyalkyl derivatives as their tetrafluoroborate or hexafluorophosphate salts $[\text{C}_6\text{H}_6\text{C}\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_2\text{OH}\}(\text{C}_6\text{Me}_6)_2(\text{O})][\text{PF}_6]$ and $[\text{C}_6\text{H}_6\text{C}\text{H}_3\text{Ru}_3\{\text{C}_6\text{H}_5(\text{CH}_2)_3\text{OH}\}(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$.^[3] However, on the basis of the data obtained so far,^[4] we cannot exclude catalysis by "soluble" metallic species (nanoclusters or colloids), and we are presently engaged in a collaborative effort to refute or support this alternative hypothesis.^[5a] In this context, we also tried to design new trinuclear arene-ruthenium cluster cations with functional substituents at

one η^6 -moiety which could give rise to more stable catalysts which may be particularly active or selective.

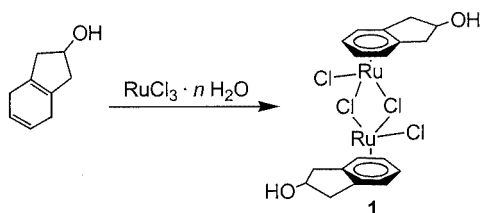
Herein we report the synthesis and characterisation of a new chloro-bridged arene-ruthenium dimer, $[\text{RuCl}_2(\textit{indanol})]_2$ (**1**), which is used to synthesise a trinuclear cluster cation containing indanol as one of the three arene ligands: $[\text{H}_3\text{Ru}_3(\textit{indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3**). Surprisingly, **3** was obtained as a mixture of two isomers, **3a** and **3b**, which were easily separated by silica-gel chromatography. Single-crystal X-ray structure analyses of $[\mathbf{3a}][\text{BF}_4]$ and $[\mathbf{3b}][\text{BF}_4]$ have been performed to establish unambiguously the molecular structures of these two isomers. The different catalytic activities of **3a** and **3b** in the hydrogenation of benzene to cyclohexane under biphasic conditions are also discussed. This is the first time that indanol has been used as a ligand in ruthenium chemistry and that both the *endo* and the *exo* isomers of the corresponding complexes have been characterised by single-crystal X-ray crystallography.

Results and Discussion

The reaction of 2,3,4,7-tetrahydro-1*H*-inden-2-ol, accessible from the Birch reduction of commercially available 2-indanol,^[6] with ruthenium(III) chloride hydrate, in refluxing ethanol, gives the chloro-bridged dimer $[\text{RuCl}_2(\textit{indanol})]_2$ (**1**), which is obtained quantitatively as an orange powder

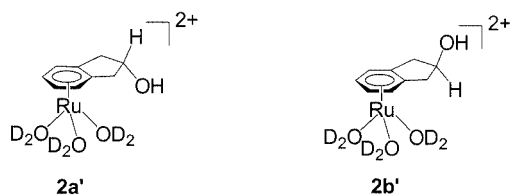
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(Scheme 1). Compound **1** is expected to exist as a mixture of three possible isomers, since the OH groups of the two indanol ligands may be folded outwards (*exo*) or inwards (*endo*). Unfortunately, as **1** is insoluble in all solvents except water and dimethyl sulfoxide, in which **1** decomposes to give mononuclear species, we cannot tell whether or not the orange powder of **1** contains only one or all three possible isomers *exo,exo-1*, *exo,endo-1* and *endo,endo-1*. The molecular formula $[\text{RuCl}_2(\text{indanol})]_2$ for **1** has been confirmed by electrospray-mass spectroscopy and micro-analysis.



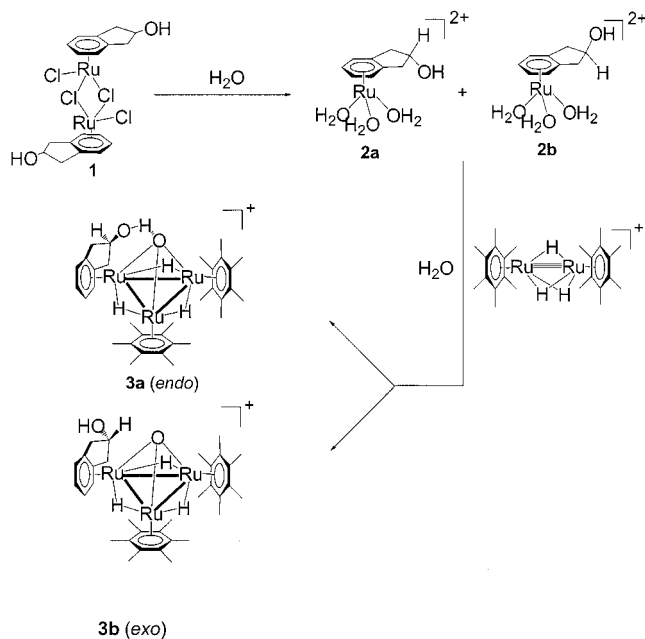
Scheme 1

In aqueous solution, the dimer **1** seems to form the mononuclear complex $[\text{Ru}(\text{indanol})(\text{H}_2\text{O})_3]^{2+}$ (**2**), an analogue of the known cation $[\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$.^[7] In order to characterise this intermediate by NMR spectroscopy, we prepared the deuterated analogue $[\text{Ru}(\text{indanol})(\text{D}_2\text{O})_3]^{2+}$ (**2'**) by cleavage of **1** with two equivalents of Ag_2SO_4 in deuterated water. The ^1H NMR spectrum of the solution obtained after elimination of the AgCl precipitate shows the expected two sets of well-defined signals which can be assigned to the two isomers $[\text{Ru}(\text{endo-indanol})(\text{D}_2\text{O})_3]^{2+}$ (**2a'**) and $[\text{Ru}(\text{exo-indanol})(\text{D}_2\text{O})_3]^{2+}$ (**2b'**) in a 10:7 ratio (Scheme 2).



Scheme 2

In aqueous solution, the mononuclear intermediate **2** (a mixture of isomers **2a** and **2b**) reacts with the dinuclear complex $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$ ^[8] to give a trinuclear arene-ruthenium cluster as a mixture of two isomers, the cations $[\text{H}_3\text{Ru}_3(\text{endo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3a**) and $[\text{H}_3\text{Ru}_3(\text{exo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3b**), in a 1:1 ratio. The oxo cap in the clusters **3a** and **3b** seems to arise from one of the H_2O ligands in the precursors **2a** and **2b**. The hydroxy function of the indanol ligand is oriented towards the μ_3 -oxo cap of **3a**, whereas it is bent away from the metal skeleton of **3b** (Scheme 3). Compounds **3a** and **3b** are easily separated as their tetrafluoroborate salts by preparative thin-layer silica-gel chromatography.



Scheme 3

Like the known analogues $[\text{H}_3\text{Ru}_3(\eta^6\text{-arene})(\eta^6\text{-arene}')_2(\text{O})]^+$,^[1,3,9] compounds **3a** and **3b** also give rise to two hydride signals each in the ^1H NMR spectra, a triplet centred at $\delta = -19.92$ ppm for **3a** and $\delta = -20.07$ ppm for **3b** and a doublet centred at $\delta = -19.30$ ppm for **3a** and $\delta = -19.41$ ppm for **3b**, integrating for one and two protons, respectively. The isolated compounds $[\mathbf{3a}][\text{BF}_4]$ and $[\mathbf{3b}][\text{BF}_4]$ were analysed by single-crystal X-ray crystallography. The molecular structures of $[\mathbf{3a}]^+$ and $[\mathbf{3b}]^+$ are shown in Figure 1.

While $[\mathbf{3b}][\text{BF}_4]$ crystallises in a monoclinic space group with one cation and one anion in the asymmetric unit, in the case of **3a** (triclinic space group) the asymmetric unit comprises two independent cations and two anions, two dichloromethane molecules, and half a molecule of dichloromethane disordered with half a water molecule. Only one molecule of **3a** is shown in Figure 1 as the other one is identical.

In both **3a** and **3b** the metal core consists of three ruthenium atoms, the three Ru–Ru distances being in accordance with a metal–metal single bond. The three ruthenium atoms are capped by a μ_3 -oxo ligand which is almost symmetrically coordinated. Selected bond lengths and angles are listed in Table 1 and 2 for **3a** and **3b**, respectively. The indanol ligand adopts an envelope conformation in which the five-membered ring is folded towards the ruthenium atom. The *endo* conformation of the indanol ligand in **3a** allows a strong intramolecular hydrogen bond between the hydroxyl substituent and the μ_3 -oxo cap, the distances between the oxygen atoms and the hydroxide protons being 1.90 Å for molecule 1 and 1.84 Å for molecule 2. The triruthenium framework of the *exo* conformation in **3b** shows intermolecular hydrogen bonds between the indanol ligand and the tetrafluoroborate ion, the distances between the hy-

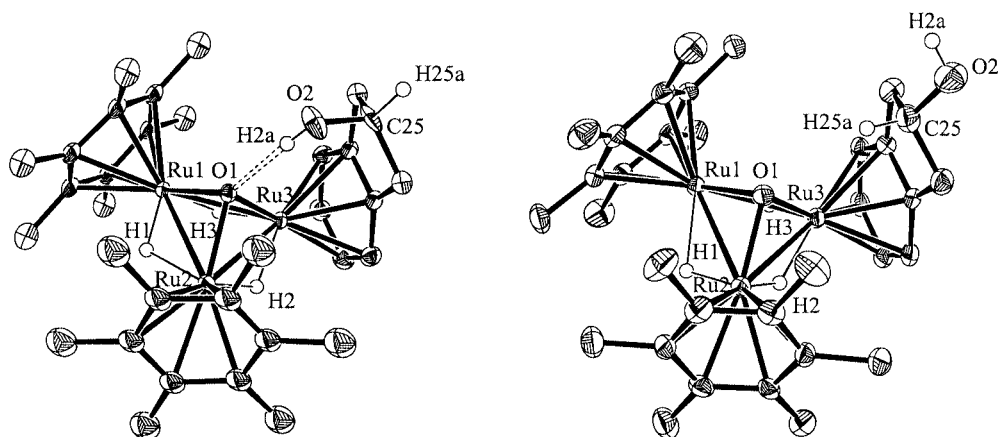


Figure 1. ORTEP views of **[3a]⁺** (left) and **[3b]⁺** (right) with displacement ellipsoids at the 50% probability level; hydrogen atoms, except for the hydroxide proton, the three hydrido ligands and the α -hydrogen atom of the indanol moiety, are omitted for clarity

Table 1. Selected bond lengths (Å) and angles (°) in **[3a][BF₄]**·1.25CH₂Cl₂·0.25H₂O

Interatomic distances		Bond angles	
Ru(1)–Ru(2)	2.7892(7)	Ru(1)–Ru(2)–Ru(3)	59.053(17)
Ru(2)–Ru(3)	2.7565(7)	Ru(1)–Ru(3)–Ru(2)	61.069(18)
Ru(1)–Ru(3)	2.7332(6)	Ru(2)–Ru(1)–Ru(3)	59.878(17)
Ru(4)–Ru(5)	2.7978(6)	Ru(4)–Ru(5)–Ru(6)	59.338(17)
Ru(5)–Ru(6)	2.7627(7)	Ru(4)–Ru(6)–Ru(5)	60.965(18)
Ru(4)–Ru(6)	2.7525(7)	Ru(5)–Ru(4)–Ru(6)	59.697(18)
Ru(1)–O(1)	2.014(4)	Ru(1)–O(1)–Ru(2)	87.70(14)
Ru(2)–O(1)	2.012(4)	Ru(1)–O(1)–Ru(3)	85.43(14)
Ru(3)–O(1)	2.015(4)	Ru(2)–O(1)–Ru(3)	86.41(14)
Ru(4)–O(3)	2.009(4)	Ru(4)–O(3)–Ru(5)	88.45(15)
Ru(5)–O(3)	2.003(4)	Ru(4)–O(3)–Ru(6)	86.35(13)
Ru(6)–O(3)	2.014(4)	Ru(5)–O(3)–Ru(6)	86.90(15)
Ru(1)–H(1)	1.4313	H(1)–Ru(1)–H(3)	92.8
Ru(2)–H(1)	1.9805	H(1)–Ru(2)–H(2)	86.5
Ru(2)–H(2)	1.8025	H(2)–Ru(3)–H(3)	85.9
Ru(3)–H(2)	1.6113	H(4)–Ru(4)–H(6)	81.4
Ru(1)–H(3)	1.6563	H(4)–Ru(5)–H(5)	79.2
Ru(3)–H(3)	1.6218	H(5)–Ru(6)–H(6)	83.9
Ru(4)–H(4)	1.8259		
Ru(5)–H(4)	1.5825		
Ru(5)–H(5)	1.6071		
Ru(6)–H(5)	1.8146		
Ru(4)–H(6)	1.4543		
Ru(6)–H(6)	1.9076		

droxide proton and two of the fluorine atoms being 2.44 Å and 2.25 Å.

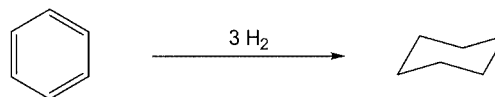
The strong intramolecular hydrogen bond found in the solid state for **3a** seems to persist also in acetone solution. The ¹H NMR spectrum of **3a** in [D₆]acetone shows a well-defined doublet centred at $\delta = 6.77$ ppm, attributed to the proton of the OH group coupled to the α -proton of the indanol ligand, the coupling constant being 13 Hz. On the other hand, the ¹H NMR spectrum of **3b** in [D₆]acetone shows a badly defined doublet centred at $\delta = 4.44$ ppm for the OH group, the coupling constant being 4.48 Hz (see Figure 2).

The water-soluble cations **3a** and **3b** are indeed found to be catalytically active for the hydrogenation of benzene to

Table 2. Selected bond lengths (Å) and angles (°) in **[3b][BF₄]**

Interatomic distances		Bond angles	
Ru(1)–Ru(2)	2.7717(9)	Ru(1)–Ru(2)–Ru(3)	59.59(2)
Ru(2)–Ru(3)	2.7437(9)	Ru(1)–Ru(3)–Ru(2)	60.72(2)
Ru(1)–Ru(3)	2.7405(8)	Ru(2)–Ru(1)–Ru(3)	59.70(2)
Ru(1)–O(1)	1.994(5)	Ru(1)–O(1)–Ru(2)	88.4(2)
Ru(2)–O(1)	1.980(5)	Ru(1)–O(1)–Ru(3)	86.7(2)
Ru(3)–O(1)	1.997(5)	Ru(2)–O(1)–Ru(3)	87.2(2)
Ru(1)–H(1)	1.8944	H(1)–Ru(1)–H(3)	89.9
Ru(2)–H(1)	1.5997	H(1)–Ru(2)–H(2)	90.6
Ru(2)–H(2)	1.2305	H(2)–Ru(3)–H(3)	95.4
Ru(3)–H(2)	1.7800		
Ru(1)–H(3)	2.0056		
Ru(3)–H(3)	1.3846		

cyclohexane under biphasic conditions; they show a catalytic activity of 67 and 125 h⁻¹ (average TOF), respectively, for a catalyst/substrate ratio of 1:1000, at 110 °C under 60 bar of H₂ during three hours. The catalytic activity of **3a** and **3b** is not as high as that of the benzene analogue [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺, which under the same conditions has an average catalytic turnover frequency of 296 h⁻¹.^[4]



After a catalytic run the cationic clusters **3a** or **3b** can be recovered unchanged from the aqueous phase in 90 to 95% yield. As a small quantity of black solid (presumably metallic ruthenium) is formed during the catalytic run, it is certainly possible, if not probable,^[5a,5b] that the catalytic reaction involves highly dispersed metallic species (“nanoclusters”) formed by partial degradation of the catalyst precursor under hydrogen pressure. The difference in the catalytic activity of **3a** and **3b** could be due to the different stability of these clusters with respect to the formation of nanopart-

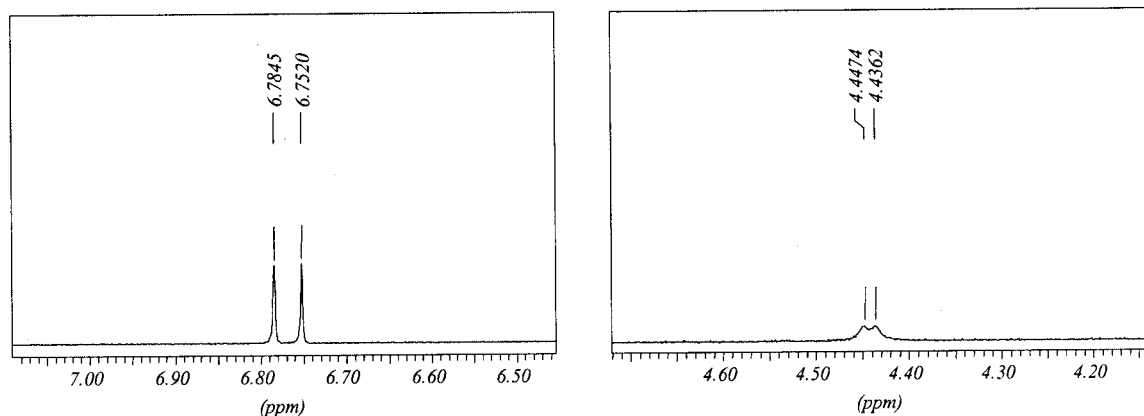


Figure 2. ^1H NMR spectra (*OH* signals) of **3a** (left) and **3b** (right) in $[\text{D}_6]\text{acetone}$ (400 MHz)

icles under the catalytic conditions. Further work is underway in order to answer this question unequivocally.^[5a]

Conclusion

Indanol, $\text{C}_9\text{H}_9\text{OH}$, has been used as a ligand in ruthenium chemistry for the first time. The new dimeric complex $[\text{RuCl}_2(\text{indanol})]_2$ (**1**) serves as a dinuclear building block for the assembly of the isomeric trinuclear cluster cations $[\text{H}_3\text{Ru}_3(\text{endo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3a**) and $[\text{H}_3\text{Ru}_3(\text{exo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**3b**), isolated as their tetrafluoroborate salts. For the first time, both *endo* and *exo* isomers of a ruthenium indanol complex have been characterised by X-ray crystallography.

Experimental Section

General Remarks: All manipulations were carried out under an inert argon atmosphere using standard Schlenk techniques. 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. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, Inc. NMR spectra were recorded using a Bruker 400 MHz spectrometer and treated using the 1D WIN NMR spectroscopy software. The mass spectra were recorded at the University of Fribourg by Prof. Titus Jenny. Microanalyses were carried out by the Mikroelementaranalytisches Laboratorium, ETH Zürich (Switzerland). 2,3,4,7-Tetrahydro-1*H*-inden-2-ol was prepared by sodium reduction of 2-indanol in liquid ammonia.^[6] The starting dinuclear dichloro complex $[\text{RuCl}_2(\text{C}_6\text{Me}_6)_2]$ was synthesised according to published methods.^[10]

$[\text{RuCl}_2(\text{indanol})]_2$ (1**):** 2,3,4,7-Tetrahydro-1*H*-inden-2-ol (6 g, 44.4 mmol) was added to a solution of ruthenium trichloride hydrate (1.70 g, 6.5 mmol) in absolute degassed ethanol (100 mL) and the mixture was refluxed overnight. After cooling to room temperature, the resulting orange precipitate was filtered, washed with diethyl ether, and dried under vacuum to give pure $[\text{RuCl}_2(\text{indanol})]_2$ as an orange powder. Yield: 1.90 g (95%). $\text{C}_{18}\text{H}_{20}\text{Cl}_4\text{O}_2\text{Ru}_2$

(612.30); calcd. C 35.31, H 3.29; found C 35.22, H 3.44. MS (ESI positive mode, methanol): $m/z = 576.8$ $[\text{M} - \text{Cl}]^+$.

$[\text{Ru}(\text{endo-indanol})(\text{D}_2\text{O})_3]^{2+}$ (2a'**) and $[\text{Ru}(\text{exo-indanol})(\text{D}_2\text{O})_3]^{2+}$ (**2b'**):** In a 250 mL brown-glass Schlenk tube, compound **1** (150 mg, 0.245 mmol) was mixed with a solution of Ag_2SO_4 (153 mg, 0.490 mmol) in 5 mL of D_2O . The suspension was stirred at room temperature until the orange solid had completely dissolved to give a yellow solution of **2a'** and **2b'**. The white precipitate of AgCl formed was removed from the aqueous solution by filtration through filter pulp and the resulting clear solution was directly analysed by NMR spectroscopy. ^1H NMR spectroscopic data for the mixture of **2a'** and **2b'** (400 MHz, D_2O , 25 °C): $\delta = 2.53$ [dd, $^2J = 16.38$, $^3J = 7.30$ Hz, 2 H, $(\text{CH})_2\text{CHOH}$], 2.81 [d, $^2J = 17.79$ Hz, 2 H, $(\text{CH})_2\text{CHOH}$], 2.98 [dd, $^2J = 17.79$, $^3J = 5.50$ Hz, 2 H, $(\text{CH})_2\text{CHOH}$], 3.17 [dd, $^2J = 16.38$, $^3J = 7.17$ Hz, 2 H, $(\text{CH})_2\text{CHOH}$], 4.83 [m, 1 H, $(\text{CH})_2\text{CHOH}$], 4.89 [m, 1 H, $(\text{CH})_2\text{CHOH}$], 5.83 to 6.00 (m, 8 H, H_{arom}) ppm.

$[\text{H}_3\text{Ru}_3(\text{endo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$ (cation **3a) and $[\text{H}_3\text{Ru}_3(\text{exo-indanol})(\text{C}_6\text{Me}_6)_2(\text{O})][\text{BF}_4]$ (cation **3b**):** In a 250 mL brown-glass Schlenk tube, $[\text{RuCl}_2(\text{C}_6\text{Me}_6)_2]$ (300 mg, 0.449 mmol) was mixed with a solution of Ag_2SO_4 (282 mg, 0.904 mmol) in 30 mL of water. The suspension was stirred at room temperature until the orange solid had completely dissolved to give a yellow solution of $[\text{Ru}(\text{C}_6\text{Me}_6)(\text{H}_2\text{O})_3]^{2+}$ (ca. 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 minutes. In a separate 50 mL Schlenk tube, NaBH_4 (75 mg, 1.974 mmol) was dissolved in 15 mL of water at room temperature. After stirring for five minutes, the NaBH_4 solution was transferred very slowly through a cannula into the 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. Solid $[\text{RuCl}_2(\text{indanol})]_2$ (260 mg, 0.425 mmol) was added to the dark clear solution containing $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$. The mixture was stirred at room temperature until the orange solid had completely dissolved. The solution was then transferred under argon into a 300 mL closed Schlenk pressure-tube and stirred under argon pressure (two atmospheres) at 60 °C for 4 d. During this time the colour of the solution changed from black to red. After cooling to room temperature, the red solution containing **3a** and **3b** was filtered through filter pulp. A large excess (200 mg) of solid NaBF_4 was then added

to the filtrate in order to precipitate the mixture of [3a][BF₄] and [3b][BF₄]. After stirring for one hour at room temperature, the red precipitate was centrifuged at 1500 rpm for 10 min and the aqueous solution was then removed from the centrifuge tube with a glass pipette. The red solid was dissolved in CH₂Cl₂ and again filtered through filter pulp, in order to eliminate unreacted NaBF₄. The solution was then concentrated to 15 mL in vacuo. The resulting concentrate was subjected to preparative thin-layer chromatography on silica-gel using CH₂Cl₂/acetone (2:1) as eluent. The pure compounds were extracted with acetone from the first ([3a][BF₄]) and the second ([3b][BF₄]) red bands. Evaporation of acetone under vacuum gave 62 mg of [3a][BF₄] and 65 mg of [3b][BF₄] as red powders (total yield: 32%). Crystals suitable for X-ray diffraction analyses were grown by slow diffusion of hexane into a CH₂Cl₂ solution of [3a][BF₄] or an acetone solution of [3b][BF₄]. C₃₃H₄₉BF₄O₂Ru₃ ([3a][BF₄]) (867.76): calcd. C 45.68, H 5.69; found C 45.42, H 5.81. C₃₃H₄₉B₁F₄O₂Ru₃ ([3b][BF₄]) (867.76): calcd. C 45.68, H 5.69; found C 45.44, H 5.87.

Spectroscopic Data for 3a: ¹H NMR (400 MHz, [D₆]acetone, 25 °C): δ = -19.92 (t, ²J = 3.83 Hz, 1 H, hydride), -19.30 (d, ²J = 3.83 Hz, 2 H, hydride), 2.34 [s, 36 H, C₆(CH₃)₆], 2.43 [d, ²J = 16.73 Hz, 2 H, (CH)₂CHOH], 3.02 [dd, ²J = 16.73, ³J = 5.54 Hz, 2 H, (CH)₂CHOH], 4.52 [m, 1 H, (CH)₂CHOH], 5.69 [dd, ³J = 3.83, ⁴J = 2.13 Hz, 2 H, H_{arom}], 5.96 [dd, ³J = 3.83, ⁴J = 2.13 Hz, 2 H, H_{arom}], 6.77 [d, ³J = 13.00 Hz, 1 H, (CH)₂CHOH] ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 25 °C): δ = 18.2 [C₆(CH₃)₆], 40.8 [(CH)₂CHOH], 70.8 [(CH)₂CHOH], 78.0, 82.8, 95.3, 101.8 (C_{arom}) ppm. MS (ESI positive mode, acetone): m/z = 782.1 [M + H]⁺.

Spectroscopic Data for 3b: ¹H NMR (400 MHz, [D₆]acetone, 25 °C): δ = -20.07 (t, ²J = 4.05 Hz, 1 H, hydride), -19.41 (d, ²J = 4.05 Hz, 2 H, hydride), 2.32 [s, 36 H, C₆(CH₃)₆], 2.69 [dd, ²J = 14.92, ³J = 7.88 Hz, 2 H, (CH)₂CHOH], 2.87 [dd, ²J = 14.92, ³J = 6.82 Hz, 2 H, (CH)₂CHOH], 4.44 [d, ³J = 4.48 Hz, 1 H, (CH)₂CHOH], 4.84 [m, 1 H, (CH)₂CHOH], 5.53 [dd, ³J = 3.83, ⁴J = 2.23 Hz, 2 H, H_{arom}], 5.84 [dd, ³J = 3.83, ⁴J = 2.23 Hz, 2 H, H_{arom}] ppm. ¹³C{¹H} NMR (100 MHz, CD₂Cl₂, 25 °C): δ = 18.1 [C₆(CH₃)₆], 39.8 [(CH)₂CHOH], 72.1 [(CH)₂CHOH], 79.3, 81.3, 95.1, 101.0 (C_{arom}) ppm. MS (ESI positive mode, acetone): m/z = 782.1 [M + H]⁺.

Catalytic Runs: In a typical experiment, a solution of [3a][BF₄] or [3b][BF₄] (10 mg) in 10 mL of water was placed in a 100 mL stainless-steel autoclave equipped with a glass-lined vessel, and the benzene substrate was added in a 1:1000 catalyst/substrate ratio. After purging four times with hydrogen, the autoclave was pressurised with hydrogen (60 bar), heated to 110 °C in an oil bath for 15 minutes, and the mixture stirred vigorously. After 3 h the autoclave was cooled in an ice-bath and the pressure released. The two-phase system was separated by decanting. The aqueous phase containing the catalyst was discarded and the organic phase containing cyclohexane and benzene was analysed by NMR spectroscopy and GC.

X-ray Crystallographic Study

[3a][BF₄].1.25CH₂Cl₂.0.25H₂O: A red crystal of [3a][BF₄].1.25CH₂Cl₂.0.25H₂O was mounted on a Stoe Imaging Plate Diffractometer System (Stoe & Cie, 1995) equipped with a one-circle φ goniometer and a graphite-monochromator. Data collection was

Table 3. Crystallographic data for the structures of {[3a][BF₄]}₂·2.5 CH₂Cl₂·0.5H₂O and [3b][BF₄]

	{[3a][BF ₄]} ₂ ·2.5 CH ₂ Cl ₂ ·0.5H ₂ O	[3b][BF ₄]
Empirical formula	C _{34.25} H ₅₂ O _{2.25} Ru ₃ BF ₄ Cl _{2.50}	C ₃₃ H ₄₉ O ₂ Ru ₃ BF ₄
Molecular mass	978.40	867.74
Crystal colour and shape	red block	orange needle
Crystal size	0.300 × 0.200 × 0.100	0.400 × 0.183 × 0.050
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	15.4090(11)	8.6447(6)
<i>b</i> (Å)	16.5547(12)	17.7673(7)
<i>c</i> (Å)	18.0306(13)	21.0089(14)
<i>a</i> (°)	116.023 (8)	90.00
<i>β</i> (°)	111.549(8)	97.543(5)
<i>γ</i> (°)	90.509(9)	90.00
<i>V</i> (Å ³)	3763.9(5)	3198.9(3)
<i>Z</i>	4	4
<i>D</i> _{calc} (g·cm ⁻³)	1.727	1.802
<i>μ</i> (Mo- <i>K</i> _α) (mm ⁻¹)	1.416	1.451
Temperature (K)	153(2)	153(2)
<i>F</i> (000)	1964	1744
Scan range (°)	2.28 < <i>θ</i> < 25.90	1.95 < <i>θ</i> < 29.55
Cell refinement parameters reflections	8000	29717
Reflections measured	28873	46056
Independent reflections	13696	8868
Reflections observed [<i>I</i> > 2σ(<i>I</i>)]	10385	6505
<i>R</i> _{int}	0.0463	0.1220
Final <i>R</i> _{int} [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.1249 ^[a]	<i>R</i> ₁ = 0.0726, <i>wR</i> ₂ = 0.1635 ^[a]
<i>R</i> _{int} (all data)	<i>R</i> ₁ = 0.0619, <i>wR</i> ₂ = 0.1392 ^[a]	<i>R</i> ₁ = 0.1013, <i>wR</i> ₂ = 0.1717 ^[a]
Goodness-of-fit	1.009	1.181
Residual density: max./min. Δρ (e ⁻ ·Å ⁻³)	1.898, -1.526	1.997, -0.983

^[a] Structure was refined on *F*_o²: *wR*₂ = {Σ[w(*F*_o² - *F*_c²)/Σw(*F*_o²)]^{1/2}, where *w*⁻¹ = [Σ(*F*_o²) + (*aP*)² + *bP*] and *P* = [max(*F*_o², 0) + 2*F*_c²]/3.

performed at $-120\text{ }^{\circ}\text{C}$ using Mo- K_{α} radiation ($\lambda = 0.71073\text{ \AA}$). 193 Exposures (3 min per exposure) were obtained at an image plate distance of 70 mm with $0 < \varphi < 193^{\circ}$ and with the crystal oscillating through 1° in θ . The resolution was $D_{\min} - D_{\max}$ 12.45–0.81 \AA .

The structure was solved by direct methods using the program SHELXS-97^[11] and refined by full-matrix least-squares on F^2 with SHELXL-97.^[12] The six hydrido ligands (H1, H2, H3, H4, H5 and H6) and the two hydrogen atoms (H5a and H5b) of the water molecule were derived from difference Fourier maps and refined with the Ru–H and O–H distances constrained to the theoretical value; the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically, except for one dichloromethane molecule which is shared with a water molecule. One BF_4 counteranion is disordered. An empirical absorption correction was applied using DIFABS (PLATON99,^[13] $T_{\min.} = 0.348$, $T_{\max.} = 0.768$).

[3b][BF₄]: An orange crystal of [3b][BF₄] was mounted on a Stoe Mark II-Imaging Plate Diffractometer System (Stoe & Cie, 2002) equipped with a graphite monochromator. Data collection was performed at $-120\text{ }^{\circ}\text{C}$ using Mo- K_{α} radiation ($\lambda = 0.71073\text{ \AA}$). 265 Exposures (3 min per exposure) were obtained at an image plate distance of 100 mm, 180 frames with $\varphi = 0^{\circ}$ and $0 < \omega < 180^{\circ}$, and 85 frames with $\varphi = 90^{\circ}$ and $0 < \omega < 85^{\circ}$, with the crystal oscillating through 1° in ω . The resolution was $D_{\min} - D_{\max}$ 17.78–0.72 \AA .

The structure was solved by direct methods using the program SHELXS-97^[11] and refined by full-matrix least-squares on F^2 with SHELXL-97.^[12] The three hydrido ligands H1, H2 and H3 were derived from difference Fourier maps and refined with the Ru–H distance constrained to the theoretical value; the remaining hydrogen atoms were included in calculated positions and treated as riding atoms using the SHELXL-97 default parameters. All non-hydrogen atoms were refined anisotropically. An empirical absorption correction was applied using DIFABS (PLATON99,^[13] $T_{\min.} = 0.139$, $T_{\max.} = 0.611$). All of the tested crystals were twinned; the structure was solved and refined on data collected from one domain of such a crystal.

Crystallographic details are given in Table 3 and significant bond lengths and bond angles are listed in Table 1 (3a) and Table 2 (3b). The figures were drawn with ORTEP.^[14]

CCDC-235554 (for [3a][BF₄] \cdot 1.25CH₂Cl₂ \cdot 0.25H₂O) and -235555 (for [3b][BF₄]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at

www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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