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An asymmetric trihydrido-bridged arene ruthenium complex

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Abstract

Reaction of $[Ru(\eta^6\text{-indane})(H_2O)_3]^{2+}$ and $[Ru(\eta^6\text{-}C_6Me_6)(H_2O)_3]^{2+}$ with $NaBH_4$ in water gives a mixture of three triple hydrido-bridged arene ruthenium cations $[(\eta^6\text{-arene})Ru(\mu\text{-}H)_3Ru(\eta^6\text{-arene}')]^+$ (arene = indane and hexamethylbenzene; arene′ = indane and hexamethylbenzene). After treatment with $NaBF_4$, the three complexes are separated by column chromatography and the asymmetrical $[(\eta^6\text{-indane})Ru(\mu\text{-}H)_3Ru(\eta^6\text{-}C_6Me_6)][BF_4]$ (cation **1a**) can be isolated in moderate yield. **1a** decomposes in solution to give the corresponding hydroxo-bridged complex $[(\eta^6\text{-indane})Ru(\mu\text{-}OH)_3Ru(\eta^6\text{-}C_6Me_6)]^+$ (**2**) with retention of the asymmetrical geometry as shown by single-crystal X-ray structure analysis. The indane ligand adopts an envelope conformation toward the ruthenium atom.

Keywords: Arene ligands; Bridging ligands; Dinuclear complexes; Hydrido; Hydroxo; Ruthenium

1. Introduction

Recently, we reported the synthesis of trinuclear ruthenium complexes $[Ru_3(\mu\text{-}H)_3(\eta^6\text{-arene})_3(O)]^+$ [1]. These water-soluble complexes, which are catalytically active in the hydrogenation of benzene to cyclohexane under biphasic conditions, are formed by reacting the corresponding dinuclear precursor $[Ru_2(\mu\text{-}H)_3(\eta^6\text{-arene})_2]^+$ [2] with the mononuclear tri-aqua cation $[Ru(\eta^6\text{-arene})(H_2O)_3]^{2+}$ [3]. In the search for new building blocks for the synthesis of catalytically active arene–ruthenium clusters, we obtained three different dinuclear trihydrido-bridged cations in one reaction step; the use of a mixture of two different arene ruthenium (arene = indane and hexamethylbenzene) precursors for the formation of $[Ru_2(\mu\text{-}H)_3(\eta^6\text{-arene})_2]^+$ affords two symmetrical and one asymmetrical dinuclear species. To the best of our knowledge, only symmetrical dinuclear hydrido-bridged arene–ruthenium complexes have been reported so far [2,4].

Herein, we present the synthesis of the first asymmetrical hydrido-bridged arene–ruthenium complex, $[(\eta^6\text{-indane})Ru(\mu\text{-}H)_3Ru(\eta^6\text{-}C_6Me_6)]^+$ (**1a**). **1a** is stable for days under an inert atmosphere, but decomposes slowly in air or in solution to form the corresponding hydroxo-bridged arene–ruthenium complex $[(\eta^6\text{-indane})Ru(\mu\text{-}OH)_3Ru(\eta^6\text{-}C_6Me_6)]^+$ (**2**), with retention of the asymmetrical geometry. The single-crystal X-ray structure analysis of $[(\eta^6\text{-indane})Ru(\mu\text{-}OH)_3Ru(\eta^6\text{-}C_6Me_6)][BF_4]$ is presented.

2. Experimental

All manipulations were carried out routinely under nitrogen atmosphere. De-ionised water and organic solvents were degassed and saturated with nitrogen prior to use. NMR spectra were recorded on a Bruker 400 MHz spectrometer. Microanalyses were carried out by the Laboratory of Pharmaceutical Chemistry, University of Geneva (Switzerland). Electro-spray mass spectra were obtained in positive-ion mode with an LCQ Finnigan mass spectrometer. The starting dinuclear dichloro complexes $[Ru(\eta^6\text{-}C_6Me_6)Cl_2]_2$ [5] and $[Ru(\eta^6\text{-indane})Cl_2]_2$ [6] were prepared according to published methods.

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2.1. *Synthesis of* $[(\eta^6\text{-indane})\text{Ru}(\mu\text{-H})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]$ $[\text{BF}_4]$ (*cation* **1a**)

A mixture of $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$ (200 mg, 0.3 mmol), $[\text{Ru}(\eta^6\text{-indane})\text{Cl}_2]_2$ (174 mg, 0.3 mmol) and Ag_2SO_4 (410 mg, 1.3 mmol) in water (40 ml) was stirred in the dark for 1 h. During this period the mixture was treated several times with ultrasound, until the orange solid was completely dissolved. The white precipitate (AgCl) was removed by filtration from the yellow solution containing $[\text{Ru}(\eta^6\text{-indane})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})_3]^{2+}$. An aqueous solution containing NaBH_4 (86 mg, 2.3 mmol, 10 ml H_2O) was added dropwise to this yellow solution. The solution turned dark-red due to the formation of the three $[\text{Ru}_2(\mu\text{-H})_3(\eta^6\text{-arene})_2]^+$ cations. After filtration, the mixture of $[\text{Ru}_2(\mu\text{-H})_3(\eta^6\text{-arene})_2][\text{BF}_4]$ precipitated from the aqueous solution by addition of an excess of NaBF_4. The green precipitate was centrifuged, dissolved in CH_2Cl_2 and filtered through celite to eliminate the excess of NaBF_4. Column chromatography on silica-gel (eluent: CH_2Cl_2/acetone 20:1) gave [**1a**][BF_4] as the second fraction. Yield: 23%.

Spectroscopic data for **1a**: ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta = 6.00$ (dd, 2H, H$_{\text{ar}}$), 5.69 (dd, 2H, H$_{\text{ar}}$), 2.69 (m, 2H, CH$_2$), 2.67 (m, 2H, CH$_2$), 2.44 (s, 18H, C$_6$(CH$_3$)$_6$), 2.07 (m, 2H, CH$_2$), −15.46 (s, 3H, Ru-hydride). MS (ESI positive mode, acetone): *m/z*: 486 $[\text{M} + \text{H}]^+$. Anal. Calc. for $\text{C}_{21}\text{H}_{31}\text{B}_1\text{F}_4\text{Ru}_2$: C, 44.06; H, 5.46. Found: C, 44.25; H, 5.41%.

2.2. *Formation of* $[(\eta^6\text{-indane})\text{Ru}(\mu\text{-OH})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]$ $[\text{BF}_4]$ (*cation* **2**)

2 was obtained by slow decomposition of **1a** in an acetone solution. After evaporation, the residue containing cation **2** was analysed by ^{1}H NMR and MS spectrometry without further purification. Crystals suitable for X-ray structure analysis were obtained from an acetone/hexane solution.

Spectroscopic data for **2**: ^{1}H NMR (400 MHz, acetone-d$_6$): $\delta = 5.32$ (dd, 2H, H$_{\text{ar}}$), 5.14 (dd, 2H, H$_{\text{ar}}$), 3.88 (s, 3H, OH), 2.72 (m, 2H, CH$_2$), 2.65 (m, 2H, CH$_2$), 2.08 (m, 2H, CH$_2$), 2.05 (s, 18H, C$_6$(CH$_3$)$_6$). MS (ESI positive mode, acetone): *m/z*: 533 $[\text{M}]^+$.

2.3. *X-ray crystallography*

X-ray data for [**2**][BF4]; $\text{C}_{21}\text{H}_{31}\text{BF}_4\text{O}_3\text{Ru}_2$, $M = 620.41$ g mol^{-1}, clinic, $P-1$ (no. 2), $a = 9.332(5)$, $b = 11.273(5)$, $c = 12.781(11)$ Å, $\alpha = 70.44(8)$, $\beta = 87.53(8)$, $\gamma = 66.04(5)°$, $U = 1150.9(12)$ Å^3, $T = 153$ K, $Z = 2$, $\mu(\text{MoK}\alpha) = 1.364$ mm^{-1}, 4133 reflections measured, 3536 unique ($R_{\text{int}} = 0.0329$) which were used in all calculations. The final wR (F^2) was 0.1036 (all data). The data were measured using a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using MoKα graphite monochromated radiation ($\lambda = 0.71073$ Å) with ϕ range 0–180°, increment of 1.8°, $D_{\max}$–$D_{\min}$ = 12.45–0.81 Å. The structure was solved by direct methods using the program SHELXS-97 [7]. The refinement and all further calculations were carried out using SHELXL-97 [8]. The oxygen atoms were treated as disordered with partial occupancy factors of 75:25. The hydrogen atoms of the hydroxo groups were not located, while the others were included in calculated positions and treated as riding atoms using the SHELXL default parameters. All non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Fig. 1 was drawn with ORTEP [9]. Full tables of atomic parameters, bond lengths and angles are deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Deposition number: [**2**][BF$_4$] 216477.

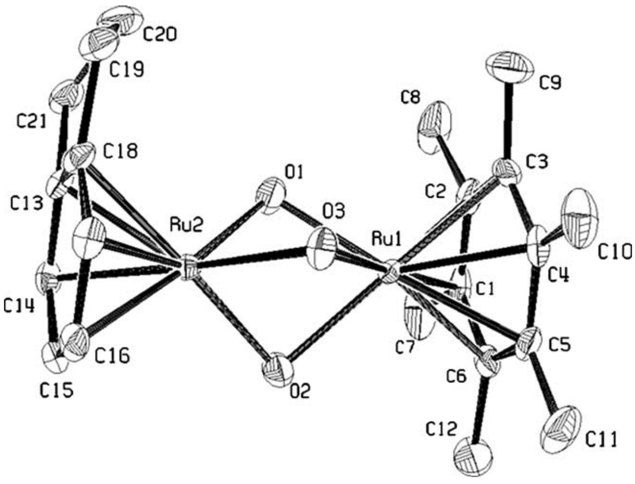
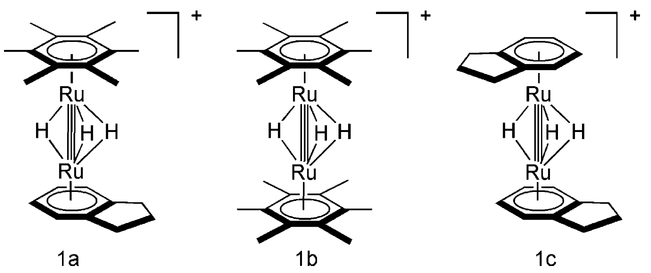


Fig. 1. ORTEP view of [**2**]$^+$, displacement ellipsoids are drawn at the 35% probability level, hydrogen atoms and BF$_4$ anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.949(4), Ru(1)–O(1) 2.080(5), Ru(1)–O(2) 2.104(5), Ru(1)–O(3) 2.066(5), Ru(2)–O(1) 2.076(5), Ru(2)–O(2) 2.082(5), Ru(2)–O(3) 2.052(5); Ru(1)–O(1)–Ru(2) 90.4(2), Ru(1)–O(2)–Ru(2) 89.6(2), Ru(1)–O(3)–Ru(2) 91.5(2).

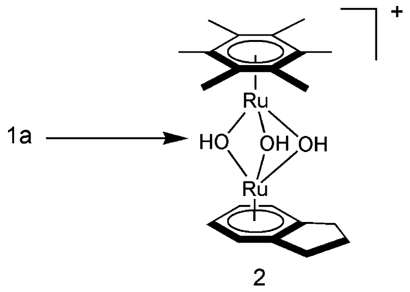
3. Results and discussion

Reaction of $[\text{Ru}(\eta^6\text{-indane})(\text{H}_2\text{O})_3]^{2+}$ and $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)(\text{H}_2\text{O})_3]^{2+}$ with NaBH_4 in water gives a mixture of three triple hydrido-bridged arene–ruthenium complexes $[(\eta^6\text{-indane})\text{Ru}(\mu\text{-H})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]^+$ **1a**, $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-H})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]^+$ **1b**, and $[(\eta^6\text{-indane})\text{Ru}(\mu\text{-H})_3\text{Ru}(\eta^6\text{-indane})]^+$ **1c**, see Scheme 1.

Surprisingly, the major components of the reaction solution are **1a** (52%) and **1b** (36%), whereas **1c** (12%) is only present as a minor compound, as demonstrated by ^{1}H NMR spectroscopy. The asymmetrical dinuclear complex **1a** is isolated as the tetrafluoroborate salt and



Scheme 1.



Scheme 2.

purified by column chromatography. When coordinated in an η^6-fashion to a metal, the two faces of the indane ligand become non-equivalent generating diastereotopic methylene protons. The ^{1}H NMR spectrum of **1a** shows a singlet ($\delta = -15.46$ ppm) in the hydride region, a singlet ($\delta = 2.44$ ppm) for the methyl groups of the hexamethylbenzene, multiplets ($\delta = 2.07$, 2.67 and 2.69 ppm) for the methylene protons, and a second series of multiplets ($\delta = 5.69$ and 6.00 ppm) for the aromatic protons of the indane ligand. The compound is stable for days under an inert atmosphere, but decomposes slowly in air or in solution to form the corresponding hydroxo-bridged complex, $[(\eta^6\text{-indane})\text{Ru}(\mu\text{-OH})_3\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)][\text{BF}_4]$ ([**2**][BF_4]), see Scheme 2. A single-crystal X-ray structure analysis of **2** was performed.

The molecular structure of [**2**]$^+$ is shown in Fig. 1. The indane ligand adopts an envelope conformation, in which the five-membered ring is folded toward the ruthenium atom. The same conformation of the indane ligand has been observed for the dinuclear complex $[\text{RuCl}_2(\eta^6\text{-indane})]_2$ [6]. The Ru–Ru distance of 2.948(4) Å is slightly shorter than those found for other triply hydroxo-bridged arene–ruthenium cations $[\text{Ru}_2(\eta^6\text{-C}_6\text{H}_6)_2(\mu\text{-OH})_3]^+$ [10] 2.9812(7), $[\text{Ru}_2(\eta^6\text{-1,3,5-C}_6\text{H}_3\text{Me}_3)_2(\mu\text{-OH})_3]^+$ [11] 2.989(3) and $[\text{Ru}_2(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})_2(\mu\text{-OH})_3]^+$ [12] 2.990(3) Å. The average bond angle for the bridging hydroxo ligands is 90.9(3)°. In the solid state, an extensive hydrogen-bonded network links the μ-OH groups to the BF_4 anions; the average O···F distances being 2.97 Å.

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