Mechanistic *in situ* High-Pressure NMR Studies of Benzene Hydrogenation by Supramolecular Cluster Catalysis with $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2][BF_4]$

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Abstract: *In situ* high-pressure NMR spectroscopy of the hydrogenation of benzene to give cyclohexane, catalysed by the cluster cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2]^+$ **2**, supports a mechanism involving a supramolecular host-guest complex of the substrate molecule in the hydrophobic pocket of the intact cluster molecule.

Keywords: benzene hydrogenation; biphasic conditions; high-pressure NMR spectroscopy; supramolecular cluster catalysis

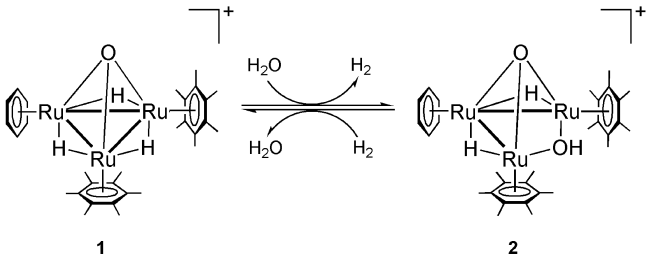
Introduction

Recently we discovered that the water-soluble cluster cations $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}H)_3]^+$ **1** and $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2]^+$ **2** are highly active in the catalytic hydrogenation of benzene to cyclohexane under biphasic conditions.[1] Mass spectroscopic studies and modelling studies support the hypothesis that the substrate molecule is incorporated in the hydrophobic pocket spanned by the three arene ligands in **1** and in **2**, suggesting the catalytic reaction to occur within this host-guest complex without the substrate being coordinated to a metal centre.[2]

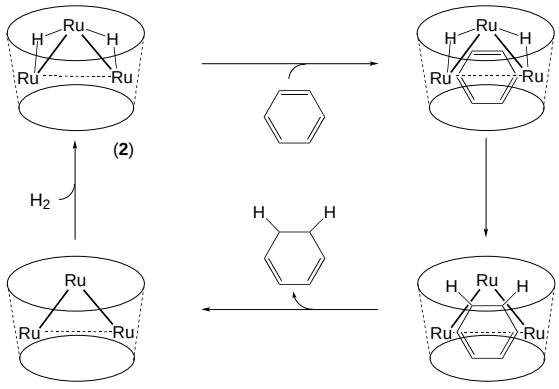
This new catalytic phenomenon, for which we coined the term "supramolecular cluster catalysis", relies entirely on weak intermolecular interactions between substrate and catalyst molecules, thus violating the mechanistic doctrine of organometallic catalysis[3] and lies at the interface between homogeneous catalysis (soluble molecular catalysts), heterogeneous catalysis (biphasic system) and enzymatic catalysis (molecular recognition).[2]

$$C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12} \qquad (1)$$

Both **1** and **2**, dissolved as tetrafluoroborate salts in water, catalyse the hydrogenation of benzene (catalyst/substrate ratio 1:10000) over a temperature range from 20 to 120 °C under hydrogen pressures between 10 and



Scheme 1. Interconversion of the cluster cations **1** and **2**.



Scheme 2. Mechanism proposed for the catalytic hydrogenation of benzene (1st hydrogenation step) within the hydrophobic pocket of cluster **2**.

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120 bar. The open cluster **2** is much more active than the closed cluster **1**. After 120 min at 100 °C and 110 bar, the catalytic turnover numbers (TON) are 488 for **1** and 9196 for **2**, the average catalytic turnover frequencies (TOF) being 244 h^{-1} and 4598 h^{-1}, respectively. At the end of the catalytic reaction, the clusters used are intact and can be reused for further runs. Both clusters **1** and **2** interconvert slowly under catalytic conditions: In aqueous solution the equilibrium is entirely on the side of **2**, while in methanol the equilibrium shifts to **1**. However, the interconversion is much slower than the catalytic hydrogenation of benzene, so that both clusters can be studied individually.

The catalytic hydrogenation of benzene, taking place at the intact cluster inside the hydrophobic pocket as illustrated for the case of **2** in Scheme 2, is supposed to proceed stepwise *via* the intermediates cyclohexadiene and cyclohexene, which are hydrogenated to give finally cyclohexane. Small amounts of the unsaturated intermediates are detected by GC-MS, if the catalytic reaction is carried out at ambient temperature; cyclohexadiene and cyclohexene employed as substrates are hydrogenated by **2** to give cyclohexane faster than benzene. The inclusion compounds (host-guest complexes) $C_6H_6 \subset$ **1** and $C_6H_6 \subset$ **2** · H_2O have been detected by electro-spray mass spectrometry.[2]

Results and Discussion

In order to rule out alternative mechanisms, we carried out an *in situ* high-pressure NMR study of the hydrogenation of benzene catalysed by **2** in deuteromethanol (C_6H_6 186.6 mg, CD_3OD 329.4 mg, **2**[BF_4] 10.2 mg, H_2 57 mg, benzene being present in excess with respect to dihydrogen). This method[4] allows the direct observation of all species involved in the catalytic process (with an abundance $> 2\%$). For the sake of resolution, the reaction was performed in a homogeneous phase (CD_3OD solution) and not under biphasic conditions.

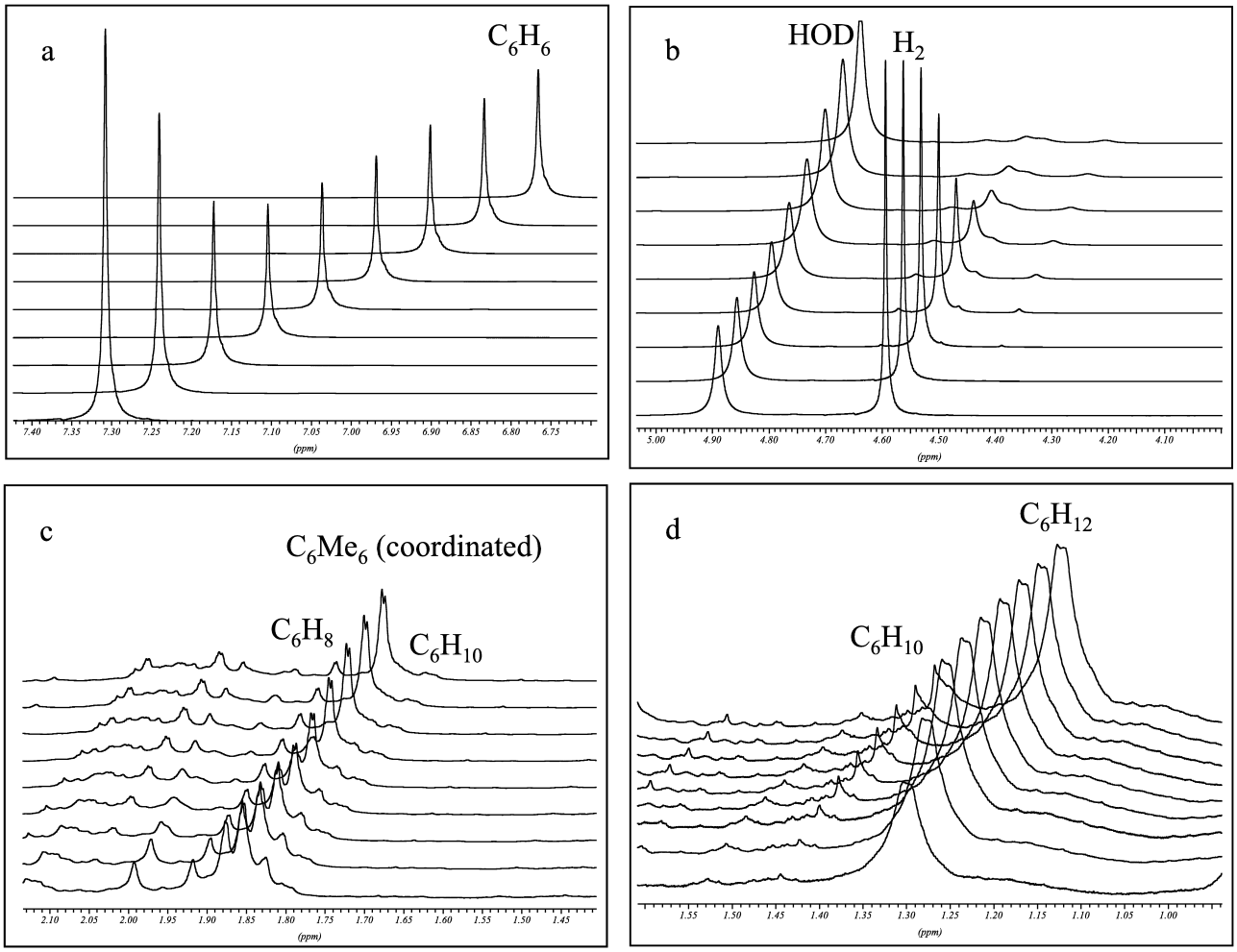

Figure 1. ^1H NMR spectra of the hydrogenation of benzene catalysed by **2** in CD_3OD solution. Conditions: CD_3OD 329.4 mg, C_6H_6 186.6 mg, H_2 57 mg (110 bar), **2**[BF_4] 10.2 mg, 26 °C. Sequence of spectra: 20 min. Spectral domains 7.40 – 6.45 ppm (**a**), 5.00 – 4.10 ppm (**b**), 2.10 – 1.45 ppm (**c**), 1.55 – 1.00 ppm (**d**).

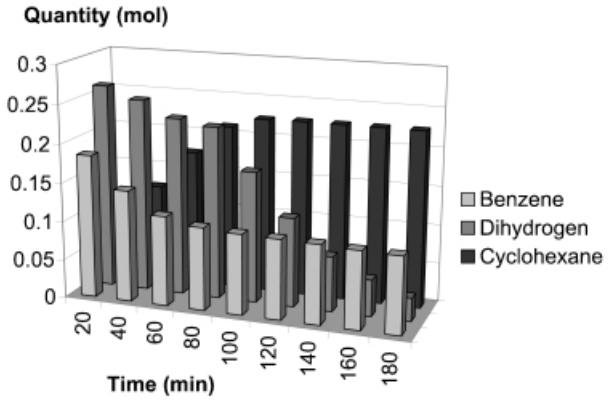

Figure 2. Evolution with time of the benzene hydrogenation at 26 °C (quantities of benzene and cyclohexane multiplied by 100 with respect that of dihydrogen).

Over a period of 48 h, 144 ^{1}H NMR spectra were recorded every 20 min at 26 °C under an initial H_2 pressure of 110 bar (corresponding to 57 mg H_2). The spectra show the signals of C_6H_6 ($\delta = 7.31$ ppm) and H_2 ($\delta = 4.59$ ppm) decreasing, while the signal of C_6H_{12} ($\delta = 1.30$ ppm) appears and increases. The signals attributed to the intermediates C_6H_8 ($\delta = 1.99$ ppm) and C_6H_{10} ($\delta = 1.45$, 1.83 ppm) appear only as small transient peaks, comparable in intensity to the methyl resonance ($\delta = 1.85$ ppm) of the two coordinated C_6Me_6 ligands in the catalyst molecule **2.** Over the whole period, hydride signals are observed in the ^{1}H NMR spectra: In the beginning (t = 0 min) the spectra show the hydride resonance of **2** at $\delta = -13.68$ (s) ppm, after the complete conversion of the substrate (t = 1 h) the characteristic hydride resonances of **1** at $\delta = -19.48$ (d) and -19.99 (t) show up, since in methanol (unlike in water) the equilibrium between **1** and **2** (Scheme 1) is shifted to the left side. During the ongoing catalytic process, several hydride signals [$\delta = -13.92$ (s), -15.48 (t), -15.54 (t) ppm] are observed subsequently, a detailed interpretation of which being impossible without further studies. On the whole, the *in situ* NMR spectra recorded are in full agreement with the mechanism proposed in Scheme 2.

We also addressed the question of water participating in the catalytic hydrogenation process by hydrogen exchange with dihydrogen. For this purpose, we studied the exchange of molecular hydrogen with D_2O in the presence of **2** as catalyst (D_2O 559 mg, **2**[BF_4] 8.0 mg, H_2 86 mg) by high-pressure ^{1}H NMR spectroscopy (100 bar, 26 °C). Indeed, we could clearly detect HD [$\delta = 4.56$ (t) ppm] and DOH ($\delta = 4.89$ ppm), which formed under the catalytic action of **2**, while the signal of

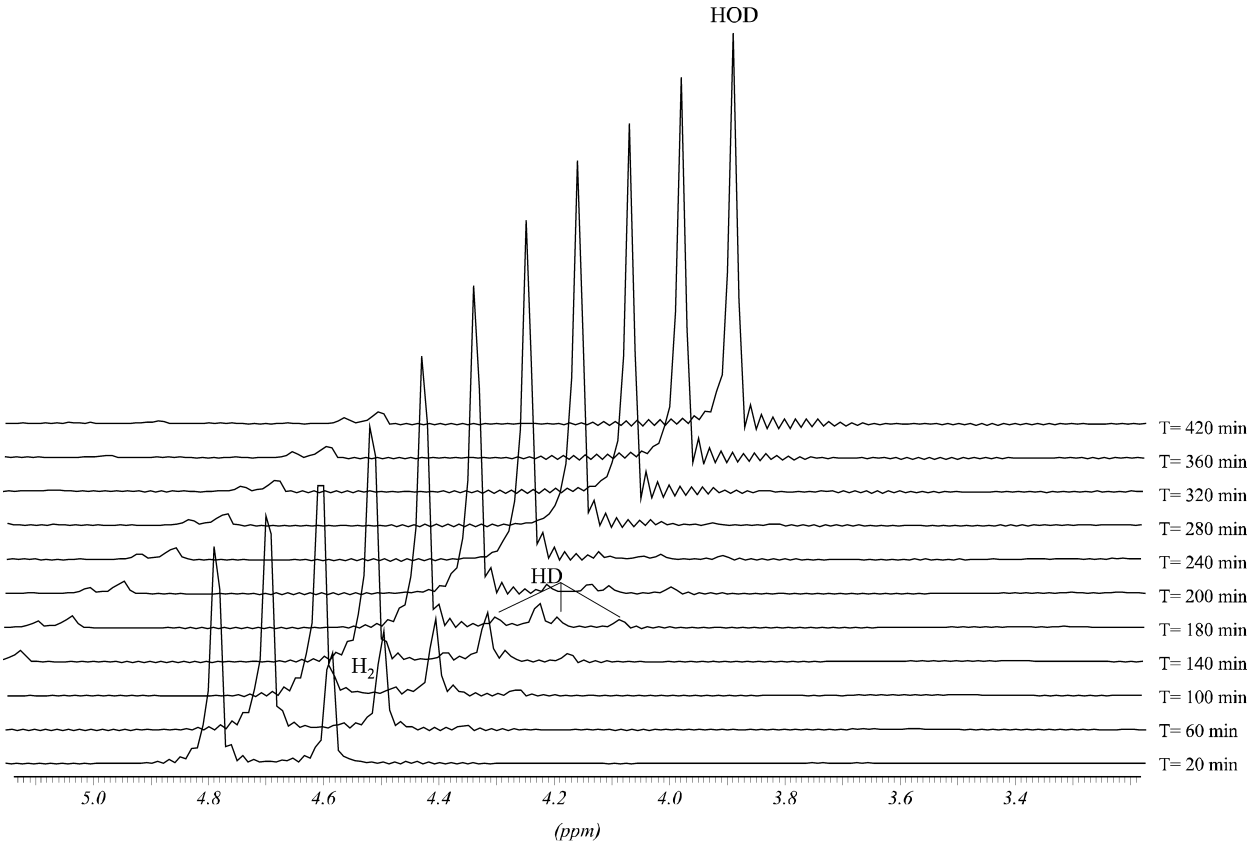

Figure 3. Hydrogen/deuterium exchange study in the reaction of H_2 with D_2O in the presence of **2** as catalyst.

H_2 ($\delta = 4.59$ ppm) disappeared slowly, as it has been observed also in the presence of other water-soluble ruthenium and rhodium complexes.[5]

$$D_2O + H_2 \longrightarrow HOD + HD \quad (2)$$

However, the H/D exchange between water and molecular hydrogen is slow as compared to the hydrogenation of benzene, both reactions being catalysed by **2**: It takes 7 h, until the H/D exchange is complete, while the benzene hydrogenation is complete after 1 h under the same conditions (26 °C, 100 bar initial hydrogen pressure). This explains why the hydrogenation of cyclohexene with D_2 to give exclusively 1,2-dideuterocyclohexane, catalysed by **2** (40 bar D_2, 100 °C, catalyst/substrate ratio 1:1000, 20 min) gives identical products in H_2O (10 mL) and in D_2O (10 mL), according to the ^1H and ^2D NMR spectra. Therefore, the implication of water in the catalytic hydrogenation of benzene, catalysed by **2** under biphasic conditions, can be neglected.

The mechanistic hypothesis of supramolecular catalysis by intact triruthenium clusters, confirmed by mercury poisoning experiments which failed in the case of **2**,[2] is further supported by the two following experiments: (i) After complete hydrogenation of C_6D_6 to give $C_6D_6H_6$ with **2**[BF_4] (catalyst/substrate 1:1000, 10 mL H_2O, 60 bar H_2, 100 °C, 6 h), the catalyst was recovered unchanged and quantitatively, the cluster cation $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2]^+$ **2** still contained one benzene and two hexamethylbenzene ligands without the benzene ligand being deuterated. This excludes any exchange between coordinated benzene and the substrate benzene. (ii) While the trinuclear cluster $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2]^+$ **2** efficiently catalyses the hydrogenation of benzene (TON 980), the mononuclear complexes $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^+$ and $[(\eta^6\text{-}C_6Me_6)Ru(H_2O)_3]^+$ are found to be almost inactive (TON 8 and 6, respectively) under the same conditions (catalyst/substrate 1:1000, 10 mL H_2O, 60 bar H_2, 110 °C, 20 min), although they contain the same arene ligands, and they are also cationic and water-soluble as the tetrafluoroborate salts. The neutral dinuclear complex $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ is also known to catalyse efficiently the hydrogenation of benzene (TON 999 after 30 min at 60 bar and 90 °C);[6] however, in this case the intermediate formation of the trinuclear cluster cation $[(\eta^6\text{-}C_6H_6)_3Ru_3(\mu_3\text{-}O)(\mu_2\text{-}Cl)(\mu_2\text{-}H)_2]^+$ **3** analogous to **2** was observed.[7] Cation **3** also contains a hydrophobic pocket, so that the high catalytic activity in this case can be explained by supramolecular cluster catalysis, too. However, unlike the hydroxo-bridged cation **2**, the chloro-bridged cation **3** is not stable under the reaction conditions and disintegrates to give finally a mixture of the tetranuclear cluster cations $[(\eta^6\text{-}C_6H_6)_4Ru_4H_4]^{2+}$ and $[(\eta^6\text{-}C_6H_6)_4Ru_4H_6]^{2+}$.[6]

The stereochemistry of the hydrogen delivery to the substrate with catalyst **2** remains to be elucidated, since deuteration studies with benzene were not conclusive: The reaction of C_6D_6 with H_2, catalysed by **2** in H_2O, gives exclusively $C_6H_6D_6$, as observed also with other catalysts,[8–10] but it was not possible to identify unambiguously the stereoisomers formed, due to the small differences in the H-D coupling constants. A detailed stereochemical study of the D_2 addition by **2** using the unsymmetrical 1-methyl-1-cyclohexene as the substrate is in progress.

Experimental Section

The compounds $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3\text{-}(\mu_3\text{-}O)(\mu_2\text{-}H)_3][BF_4]$ (cation **1**) and $[(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6Me_6)_2Ru_3(\mu_3\text{-}O)(\mu_2\text{-}OH)(\mu_2\text{-}H)_2][BF_4]$ (cation **2**) were prepared according to published methods.[1,2,11] By routine, all manipulations were carried out under nitrogen using standard Schlenk techniques, although the compounds are not air-sensitive.

The high-pressure NMR spectra were recorded with a Bruker AMX-400 instrument using a sapphire tube assembly according to published methods.[12,13]

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