

Supramolecular cluster catalysis: facts and problems

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Abstract

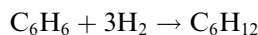
By checking the chemistry underlying the concept of “supramolecular cluster catalysis” we identified two major errors in our publications related to this topic, which are essentially due to contamination problems. (1) The conversion of the “closed” cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) into the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), which we had ascribed to a reaction with water in the presence of ethylbenzene is simply an oxidation reaction which occurs in the presence of air. (2) The higher catalytic activity observed with ethylbenzene, which we had erroneously attributed to the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), was due to the formation of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$, caused by a hydroperoxide contamination present in ethylbenzene.

Keywords: Catalysis; Ruthenium; Clusters; Hydrogenation benzene

1. Introduction

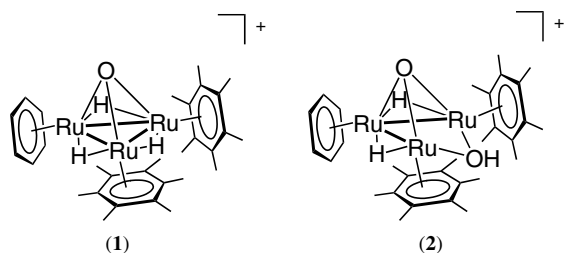
Organometallic catalysis is generally supposed to proceed through a catalytic cycle that involves the *coordination of the substrate*, either by ligand substitution or by oxidative addition, *transformation of the coordinated substrate*, and the *liberation of the product*, either by decoordination or by reductive elimination [1]. Classical examples that have been studied in great detail are the hydrogenation of olefins with Wilkinson’s catalyst [2] and the carbonylation of methanol with rhodium iodide (Monsanto Process) [3]. The complete characterisation of the intermediates of the latter process and the proposal of a well-established catalytic cycle represents one of the triumphs of organometallic chemistry [4]. In all these reactions, the elementary steps of the catalytic process are believed to occur within the *first* coordination sphere of the organometallic catalyst [5].

Only recently catalytic mechanisms without coordination of the substrate to the metal centre of the catalyst molecule have been considered [6,7], based on accumulating evidence for hydrogen transfer within merely hydrogen-bonded substrate–catalyst complexes in the case of catalytic ketone transfer hydrogenation reactions [8] and for oxygen transfer via direct olefin attack to the oxo ligand of the catalyst in epoxidation reactions [9].



We discovered in 1999 that the cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**), employed as the water-soluble tetrafluoroborate salt, efficiently catalyses the hydrogenation of benzene to cyclohexane under biphasic conditions [10]. From mass spectroscopic measurements and from molecular modelling studies, we concluded that the substrate molecule is incorporated in the hydrophobic pocket spanned by the three arene ligands in **1** (see Scheme 1), suggesting the catalytic reaction to occur within this host–guest complex without prior coordination of the substrate (“supramolecular cluster catalysis”) [11].

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Scheme 1. The “closed” cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) (48 electron species) and the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**) (50 electron species). In both cases, the three arene ligands span a hydrophobic pocket underneath the triruthenium plane.

With ethylbenzene as the substrate, we observed the catalytic activity of **1** to be higher than with benzene or other benzene derivatives. As we isolated from the aqueous phase the cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), which derives from **1** by replacing a hydrido bridge by a hydroxo bridge, we attributed the higher catalytic activity to this “open” trinuclear cluster which contains only two ruthenium–ruthenium bonds [2.780(1) Å] in accordance with the electron count of 50 [11–13].

The hydrogenation of benzene and of other aromatics has remained predominantly a field of heterogeneous catalysis [14]. Most organometallic complexes known to catalyse the homogeneous hydrogenation of olefins, ketones or acetylenes fail in the case of benzene or other aromatics; the first putative example of a homogeneous benzene hydrogenation catalyst being $(\text{C}_3\text{H}_5)\text{Co}[\text{P}(\text{OMe})_3]_3$ reported in 1974 by Muetterties [15]. Other examples include $(\text{C}_6\text{Me}_6)_2\text{Ru}$ [16], $\text{H}_2\text{Ru}_2(\text{C}_6\text{Me}_6)_2\text{Cl}_2$ [17], $\text{H}_2\text{Ru}(\text{H}_2)_2(\text{PCy}_3)_2$ [18], $[\text{H}_4\text{Ru}_4(\text{C}_6\text{H}_6)_4]\text{Cl}_2$ in water [19] or ionic liquids [20], $\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_2$ [21], $\text{Rh}_2(\text{C}_5\text{Me}_5)_2\text{Cl}_2$ in combination with NEt_3 [22]. The most significant development in the field of homogeneous benzene hydrogenation resulted in the *Dimersol* process by the Institut Français du Pétrole, based on nickel or cobalt alkoxides, acetylacetonates or carboxylates and trialkylaluminium activators [23], which appears to be a viable homogeneous alternative to the heterogeneous technology of industrial benzene hydrogenation [24]. A new generation of homogeneous arene hydrogenation catalysts on the basis of niobium and tantalum hydride derivatives have been developed by Rothwell [25], e.g. $\text{Nb}(\text{OC}_6\text{HPh}_{4-2,3,5,6})_2\text{Cl}_3$ in combination with BuLi .

For organometallic benzene hydrogenation catalysts the true nature of the catalytic species remained a debatable point (“is it homogeneous or heterogeneous catalysis?”) [26]. In the case of the putative homogeneous $[(\text{C}_8\text{H}_{17})_3\text{Me}][\text{RhCl}_4]$ ion pair catalyst [27], Finke and co-workers [28] was able to demonstrate in a pioneering paper that rhodium(0) nanoclusters are the true catalysts (“soluble heterogeneous catalysts”). On the

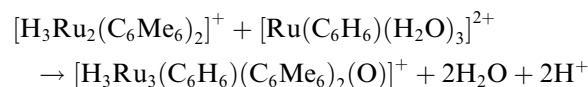
other hand, rhodium colloids obtained from a mixture of $[(\text{C}_n\text{H}_{2m+1})\text{NMe}_2(\text{CH}_2\text{CH}_2\text{OH})]\text{Br}$ with rhodium powder in water give a reusable suspension for the catalytic hydrogenation of benzene [29]. Homogeneous arene hydrogenation catalysts have been reviewed recently by Finke and Widegren [30a] and by Dyson [30b], the question of the true nature of the catalytic species in arene hydrogenation with soluble metal complexes has been critically addressed by Finke and Widegren [31].

The water-soluble cluster cations **1** and **2**, which we had reported to catalyse efficiently the hydrogenation of benzene and benzene derivatives, seem to be molecular catalysts that work under biphasic conditions and show molecular recognition for the substrate. This observation led us to suggest catalysis by the intact trinuclear cluster system, the catalytic transformations taking place inside the hydrophobic pocket [11], an interpretation which has been questioned recently [31,32]. However, last year the reported synthesis of the “open” cluster cation **2** was not longer reproducible in our hands, which forced us to check all our results in order to eliminate errors which we had made and to find evidence for the catalytic concept we had proposed. Herein we report the results of this re-investigation and a revised version of supramolecular cluster catalysis.

2. Results and discussion

2.1. The “closed” cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**): confirmation of the synthetic procedure and of the catalytic properties

The synthesis of the closed cluster $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) works as reported [10] without problems in aqueous solution: The dinuclear precursor $[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$ and the mononuclear precursor $[\text{Ru}(\text{C}_6\text{H}_6)(\text{H}_2\text{O})_3]^{2+}$ are formed in situ from $\text{Ru}_2(\text{C}_6\text{Me}_6)_2\text{Cl}_4$ and NaBH_4 and from $\text{Ru}_2(\text{C}_6\text{H}_6)_2\text{Cl}_4$ in water; cation **1** can be isolated as the tetrafluoroborate salt with the reported yield.



We then checked the catalytic properties of the water-soluble cluster cation **1**: It serves as an efficient catalyst (or possibly catalyst precursor) for the hydrogenation of benzene to give the corresponding cyclohexane under biphasic conditions (catalyst/substrate ratio 1:1000) with the catalytic activity reported [10,11]. In the case of methyl-substituted benzene derivatives, the TON and TOF values obtained under rigorously controlled conditions (Table 1) are slightly lower than the previously reported values [10]. In all cases, $[\text{BF}_4]$ can be recovered almost quantitatively (>95%) from the aqueous

Table 1

Hydrogenation of benzene and benzene derivatives catalysed by $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) under biphasic conditions^a

Substrate	Product	Time (h)	Yield ^b (%)	TON ^c	TOF ^d (h ⁻¹)
Benzene	Cyclohexane	2.5	74	740	296
Toluene	Methylcyclohexane	2.5	50	500	200
<i>p</i> -Xylene	1,4-Dimethylcyclohexane ^e	2.5	45	450	180
<i>m</i> -Xylene	1,3-Dimethylcyclohexane ^e	2.5	43	430	172
<i>o</i> -Xylene	1,2-Dimethylcyclohexane ^e	2.5	44	440	176
<i>Pseudo</i> -Cumene	1,2,4-Trimethylcyclohexane ^e	2.5	5	50	20
Durene	1,2,4,5-Tetramethylcyclohexane ^e	2.5	0	0	0

^a Conditions: H₂O 10 ml, catalyst $[\text{1}][\text{BF}_4]$ 0.01 mmol, substrate 10 mmol, H₂ pressure 60 bar, temperature 110 °C, stirring frequency 900 min⁻¹.^b Determined by gas chromatography.^c Catalytic Turnover Number: mol product formed per mol catalyst.^d (Mean) Catalytic Turnover Frequency: mol product formed per mol catalyst and per time unit.^e Mixture of *cis* and *trans* isomers.

phase after a catalytic run; the trinuclear cluster is intact and can be reused for further runs.

The catalytic activity of **1** for the hydrogenation of benzene derivatives under biphasic conditions depends predominantly on steric factors: Although methyl substituents increase the electronic density of the aromatic system, which should favour the catalytic activity, the increasing bulk of the substrate slows the catalytic reaction down: Thus, the highest catalytic activity is observed with the parent benzene substrate (TOF 290 h⁻¹). The catalytic activity is reduced for toluene with one methyl substituent (TOF 200 h⁻¹) and for the xylenes with two methyl substituents (TOF 172–180 h⁻¹). The system still tolerates three methyl substituents (TOF 20 h⁻¹ for *pseudo*-cumene), but with four methyl substituents (durene), no catalytic activity is observed. This shape-selectivity with respect to the substrate suggests molecular recognition of the substrate by the catalyst.

We studied in particular the question of arene ligand exchange between cluster **1** and the aromatic substrate during the catalytic reaction, since the mechanistic scheme of supramolecular cluster catalyst we had proposed [11,13] does not involve coordination of the aromatic substrate to a ruthenium atom of the catalyst. If the catalytic reaction is carried out with hexadeuterobenzene as the substrate under the usual biphasic conditions (catalyst/substrate ratio 1:1000, 110 °C, 60 bar), the reaction yields as expected 1, 2, 3, 4, 5, 6-hexadeuterocyclohexane, while cluster **1** still contains one C₆H₆ and two C₆Me₆ ligands (and no coordinated C₆D₆) after the catalytic reaction, according to NMR and MS data. This observation rules out an η⁶-coordination of the substrate to a metal centre in this catalytic reaction, being consistent with only supramolecular effects for the interaction between the catalyst and the substrate.

In the case of toluene hydrogenation (catalyst/substrate ratio 1:1000, 110 °C, 60 bar), the situation was not so clear: While the ¹H NMR spectrum of the organometallic residue of the aqueous phase dissolved in D₂O showed only the expected signals of **1**, the electrospray mass spectrum of the organometallic residue revealed a

small amount of the cluster $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_5\text{Me})(\text{C}_6\text{Me}_6)_2(\text{O})]^+$, in which the benzene ligand is exchanged against a toluene ligand; given that this cluster is not visible in the NMR spectrum, we estimate its content to less than 5%. We believe that the exchange of the benzene ligand in **1** by the more electron-rich toluene is a side-reaction which takes place in parallel to the catalytic toluene hydrogenation inside the hydrophobic pocket of **1**. And indeed, we observed the same exchange (less than 5%) by heating a mixture of toluene with an aqueous solution of **1** (1000:1) for 2 h to 110 °C without hydrogen pressure.

We also found the catalytic reaction to work only in the presence of water (biphasic conditions); in homogeneous phase with both, catalyst ($[\text{1}][\text{BF}_4]$) and substrate (benzene) dissolved in tetrahydrofuran/ethanol (5:1), there is no reaction. These findings are consistent with the formation of a supramolecular catalyst–substrate host–guest complex being a key species in the catalytic process.

2.2. The “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**): elucidation of the synthetic problems and rectification of the catalytic properties

The synthetic problem of the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**) turned out to be not trivial, the synthesis reported [11,12] being not longer reproducible. Variations of the temperature (20–110 °C) or the pH value (3–10) of the aqueous solution did not open the “closed” cluster cation **1** to give **2**; in all cases **1** could be recovered quantitatively, unless complete degradation of the organometallic species was observed. However, we found the solution to the problem, when we admitted air into the reaction system: The conversion of **1** into **2**, which we had formulated as a dehydrogenating hydrolysis reaction [11,12] turned out to be a simple aerobic oxidation reaction; the hydroxo bridge in **2** comes from dioxygen (air) and not from water. The reaction is best carried out in aqueous solution under atmospheric pressure of air; the complete

conversion of **1** into **2** takes 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 intermediary species.

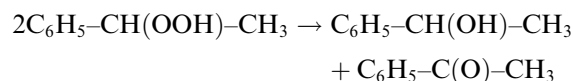
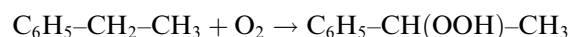
However, when we checked the catalytic activity of the “open” cluster **2** (dissolved as the tetrafluoroborate salt in water) for the hydrogenation of benzene under biphasic conditions (catalyst/substrate ratio 1:1000, 110 °C, 60 bar), we could not reproduce the higher activity we had claimed (around 3000 instead of 300 cycles per hour) [11,12]: Indeed, by using [2]BF₄ as a catalyst, benzene is hydrogenated to give cyclohexane, the catalytic activity, however, being almost the same as for [1]BF₄. This observation finds its explanation in the instability of **2** under the catalytic conditions: Under hydrogen pressure (60 bars) at 110 °C, **2** converts back quantitatively into **1** (see Fig. 1); cation **1** can be recovered at the end of the catalytic reaction as the tetrafluoroborate salt. It is therefore not surprising that, even if [2]BF₄ is used as catalyst precursor for the hydrogenation of benzene under biphasic conditions, the catalytic activity of the “closed” cluster **1** is observed after some hours, because **1** seems to be the stable species present during the catalytic run.

2.3. The contamination problem: elucidation of the increased catalytic activity by using contaminated ethylbenzene

It turned out very soon that the higher catalytic activity, which we had observed before and erroneously attributed to cluster **2** [11,12], was due to a contamina-

tion in the ethylbenzene we had used for the synthesis of **2**. The original batch of ethylbenzene showed indeed an enhanced catalytic activity of **1** (or **2**), when it was now employed as a substrate. This catalytic activity (TOF 3600 h⁻¹) could not be reproduced with rigorously purified ethylbenzene, with which we observed only the “normal” catalytic activity of [1]BF₄ of 290 h⁻¹ under the same biphasic conditions (catalyst/substrate ratio 1:1000, 110 °C, 60 bar). Thus, it became clear that the ethylbenzene we had originally used contained a contamination which served as an activator for the catalytic reaction.

The search for this activator in the contaminated ethylbenzene sample proved to be non-trivial: A GC/MS analysis of the sample revealed two major contaminants: Phenylmethylketone and 1-phenylethan-1-ol. However, neither of these two contaminants turned out to be the activator: When we added either of these compounds to the catalytic hydrogenation of benzene under biphasic conditions (catalyst/activator/substrate ratio 1:100:1000, 110 °C, 60 bar), there was essentially no effect.



Given that both contaminants found by GC/MS analysis are oxidation products of ethylbenzene [33], we considered the mechanism of the aerobic ethylbenzene oxidation [34]: Ethylbenzene is attacked by molecular oxygen from air at the methylene group to give the hydroperoxide intermediate C₆H₅-CH(OOH)-CH₃ which will then decompose to give phenylmethylketone

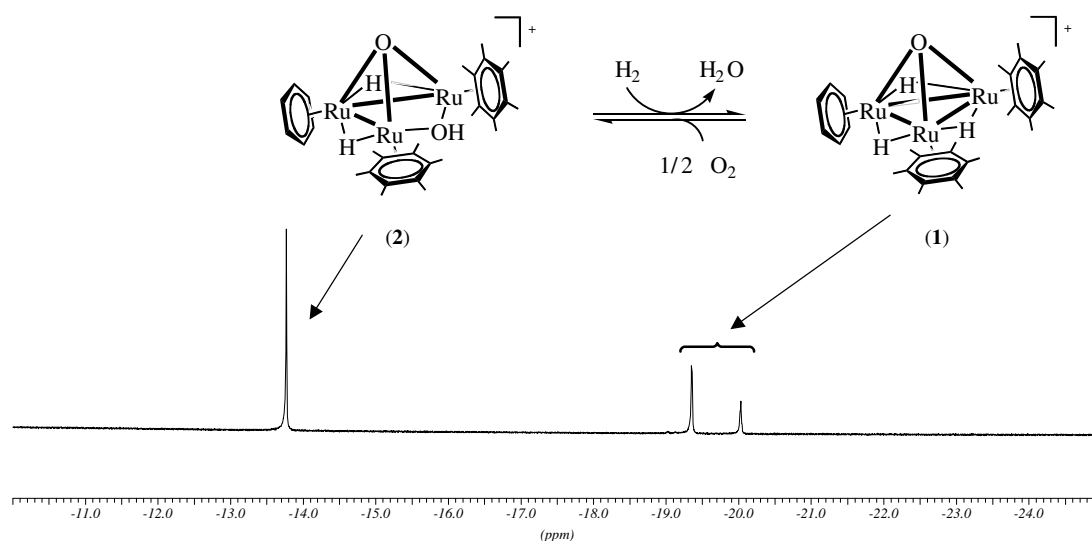


Fig. 1. Conversion of the “closed cluster **1** with molecular oxygen into the “open” cluster **2** and conversion of **2** into **1** with molecular hydrogen. The ¹H NMR spectrum shows a D₂O solution of both **1** and **2** in equilibrium. (The enlargement reveals the hydride signal of **2** being a 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.)

and 1-phenylethan-1-ol. We reasoned that, if this hydroperoxide intermediate was present in the contaminated ethylbenzene, it would not be detected by GC/MS analysis, because it would decompose on the GC column to give the two compounds observed.

Based on the idea that the activating component in the contaminated ethylbenzene is this hydroperoxide intermediate, we tested the commercially available *tert*-butylhydroperoxide as an activator for the hydrogenation of benzene, catalysed under biphasic conditions by **1**[BF₄], and we did indeed find an enhanced activity: By using an aqueous phase (10 ml) obtained from the reaction (30 min) of **1**[BF₄] (in 10 ml H₂O) with 10 equivalents of *t*-BuOOH (in decane) after washing three times with 20 ml of ether (to remove the excess of *t*-BuOOH) for the hydrogenation of benzene (catalyst/substrate ratio 1:1000, 110 °C, 60 bar), we observed a catalytic activity (TOF 3700 h⁻¹) 10 times greater than without activator. From this result, it can be concluded that the contamination, which had caused the enhanced catalytic activity, was indeed the primary ethylbenzene oxidation product C₆H₅-CH(OOH)-CH₃.

However, the aqueous phase obtained by treatment with *tert*-butylhydroperoxide (or with the contaminated ethylbenzene) did not contain **1** or other soluble organometallic species any more. It was cloudy and contained a finely dispersed dark solid, which could be filtered off and which proved to be a highly reactive heterogeneous catalyst for the hydrogenation of benzene. A second catalytic run with this solid catalyst, suspended in water, reproduced the same catalytic activity (TOF 3700 h⁻¹). The isolated solid contained 21% oxygen, suggesting the presence of hydrated ruthenium dioxide, RuO₂ · *n*H₂O, in accordance with energy dispersive X-ray spectroscopy (EDS). Scanning electron microscopy (SEM) of the aqueous phase revealed a particle size on the micro- (not nano) scale (Fig. 2).

The high catalytic activity of ruthenium dioxide, a simple inorganic solid, for the hydrogenation of benzene and benzene derivatives is due to the fact that we did the catalytic reaction under biphasic conditions. In fact, while commercial RuO₂ · *n*H₂O shows approximately the same activity for the hydrogenation of benzene without or with additional water (TOF around 3000 h⁻¹), whereas anhydrous RuO₂ was almost completely inactive (TOF 2 h⁻¹) under the same mild conditions (catalyst/substrate ratio 1:1000, 110 °C, 60 bar).

2.4. Supramolecular cluster catalysis revisited: isolation and characterisation of supramolecular catalyst–substrate host–guest complexes

In the absence of hydroperoxide contaminations, the “closed” cluster cation [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺ (**1**) catalyses the hydrogenation of benzene and benzene derivatives under biphasic conditions essentially without

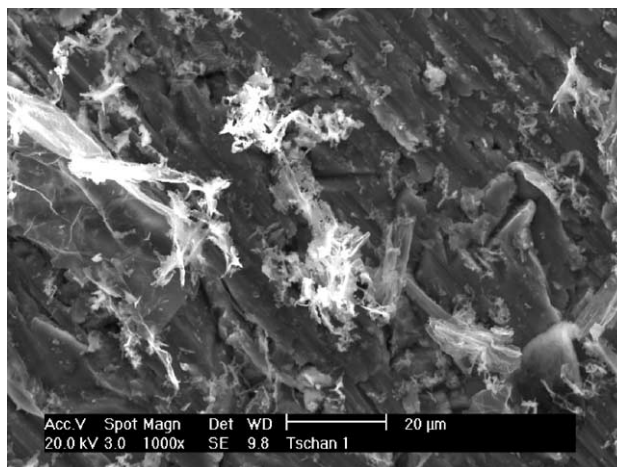


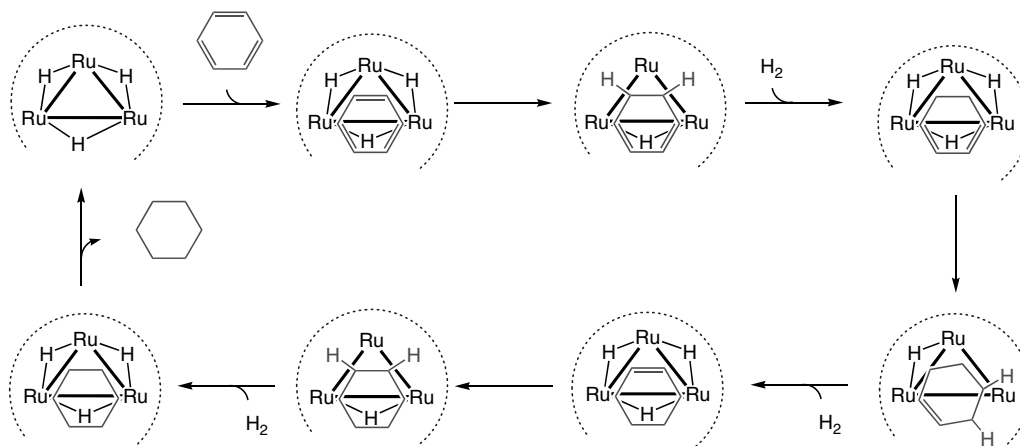
Fig. 2. Scanning electron micrograph of the aqueous phase recovered from the biphasic hydrogenation of hydroperoxide-contaminated ethylbenzene catalysed by **1**[BF₄], showing solid micro-scale particles (presumably RuO₂ · *n*H₂O).

decomposition (<5%). After a catalytic run, the clear, red, aqueous phase containing **1** can be reused for further runs.

As originally proposed [11], **1** can accommodate the substrate molecule benzene in its hydrophobic pocket formed by the three arene ligands and to place it in a perfect position underneath the Ru₃ face opposite to the oxo cap of the cluster. This is possible as, under biphasic conditions, the hydrophobic substrate tries to escape from the aqueous medium. In the resulting supramolecular catalyst–substrate host–guest complex, the substrate molecule is not coordinated to ruthenium but interacts with the Ru₃ surface only through weak intermolecular interactions.

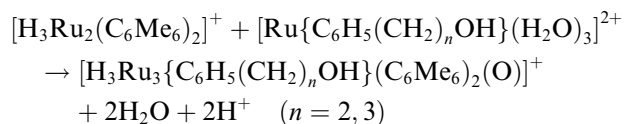
The catalytic hydrogenation is believed to occur within this supramolecular host–guest complex in a three-step mechanism (Scheme 2): Transfer of two hydrogen atoms from the cluster molecule to the substrate within the cluster–benzene complex leads to a cluster–cyclohexadiene complex, in which the unsaturated cluster [HRu₃(C₆H₆)(C₆Me₆)₂(O)]⁺ would react with molecular hydrogen to regenerate [H₃Ru₃(C₆H₆)(C₆Me₆)₂(O)]⁺ (**1**), capable of transferring two hydrogen atoms to the cyclohexadiene molecule. In the resulting cluster–cyclohexene complex, the unsaturated cluster [HRu₃(C₆H₆)(C₆Me₆)₂(O)]⁺ would again react with H₂ to regenerate **1**, which would again transfer two hydrogen atoms to the substrate. The cyclohexane formed would leave the hydrophobic pocket, while **1** is regenerated with molecular hydrogen. At the end of the catalytic reaction, **1** is recovered unchanged as the tetrafluoroborate salt.

Recently, we prepared two “closed” cluster cations analogous to **1**, [H₃Ru₃{C₆H₅(CH₂)₂OH}(C₆Me₆)₂(O)]⁺ (**3**), and [H₃Ru₃{C₆H₅(CH₂)₃OH}(C₆Me₆)₂(O)]⁺ (**4**), by analogy from the dinuclear precursor



Scheme 2. Proposed mechanism for the stepwise catalytic hydrogenation of benzene to cyclohexane within the hydrophobic pocket (dashed line) spanned by the three arene ligands of the intact trinuclear cluster **1–4** (arene ligands and oxo cap omitted for clarity).

$[\text{H}_3\text{Ru}_2(\text{C}_6\text{Me}_6)_2]^+$ and the corresponding mononuclear arene ruthenium triqua complex [35].



In these two cluster cations containing a $(\text{CH}_2)_n\text{OH}$ ($n = 2, 3$) side-arm at the benzene ligand, we were able to isolate the catalyst–substrate host–guest complexes $[\text{C}_6\text{H}_6 \subset \mathbf{3}][\text{PF}_6]$ and $[\text{C}_6\text{H}_6 \subset \mathbf{4}][\text{BF}_4]$ and to characterise these postulated supramolecular intermediates by single-crystal X-ray structure analysis [35]. A structural comparison of **3** and $[\text{C}_6\text{H}_6 \subset \mathbf{3}]^+$ shows almost identical geometrical parameters, differences appear only at the periphery (Figs. 3 and 4).

In the two catalyst–substrate complexes isolated, the substrate guest is accommodated by the catalyst host in an inclined fashion inside the hydrophobic pocket: In

$[\text{C}_6\text{H}_6 \subset \mathbf{3}]^+$, the angle formed by the C_6 plane and the Ru_3 plane is $66.78(7)^\circ$, while it is $88.63(9)^\circ$ in $[\text{C}_6\text{H}_6 \subset \mathbf{4}]^+$, the shortest distances between the metal-bound hydrogen atoms and the closest carbon atoms of the benzene guest molecule being 3.49 and 3.69 Å in $[\text{C}_6\text{H}_6 \subset \mathbf{3}]^+$, and 3.26 and 3.77 Å in $[\text{C}_6\text{H}_6 \subset \mathbf{4}]^+$ (Figs. 5 and 6).

The direct observation of the catalyst–substrate host–guest complexes was a missing link in the concept of supramolecular cluster catalysis. The isolation and the X-ray crystallographic characterisation of $[\text{C}_6\text{H}_6 \subset \mathbf{3}][\text{PF}_6]$ and $[\text{C}_6\text{H}_6 \subset \mathbf{4}][\text{BF}_4]$ demonstrate that the hypothesis of catalyst–substrate host–guest complexes as key species in the catalytic hydrogenation of benzene is not unreasonable. However, on the basis of the data obtained so far, 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 [37].

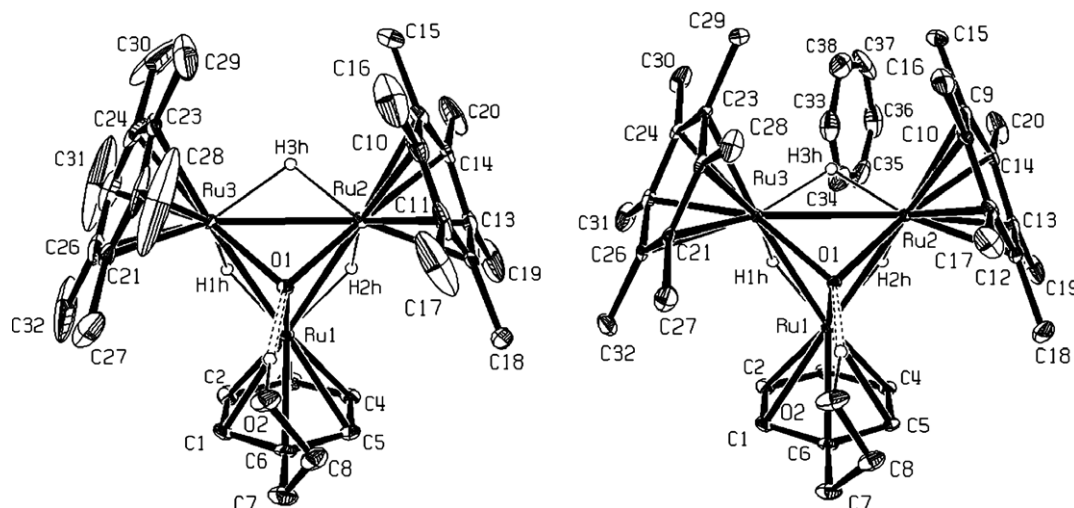


Fig. 3. Molecular structure of cation **3** and $[\text{C}_6\text{H}_6 \subset \mathbf{3}]^+$ at 25% probability level, H atoms and PF_6 omitted for clarity.

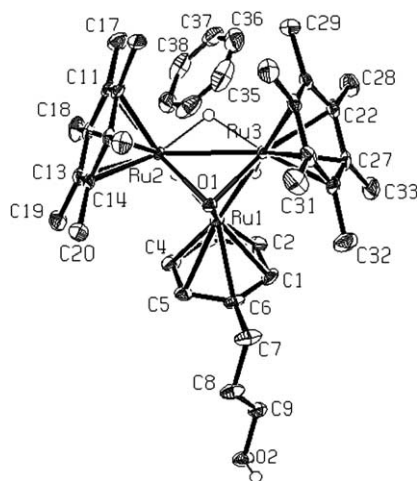


Fig. 4. Molecular structure of $[\text{C}_6\text{H}_6 \subset 4]^+$ at 25% probability level, H atoms, H_2O and BF_4 omitted for clarity.

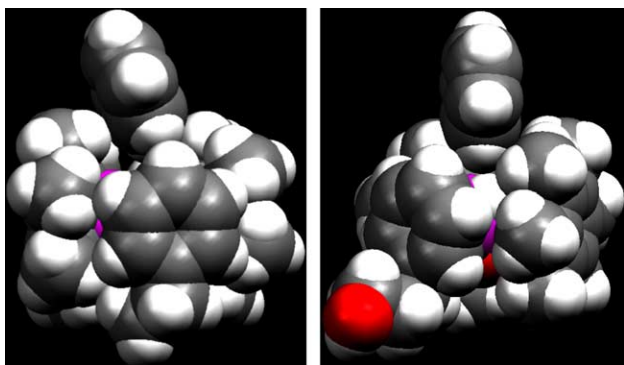


Fig. 5. Space filling representation of the host-guest complexes $[\text{C}_6\text{H}_6 \subset 3]^+$ and $[\text{C}_6\text{H}_6 \subset 4]^+$, based on the X-ray data, showing the benzene host (at the top) penetrating the hydrophobic pocket of 3 and 4.

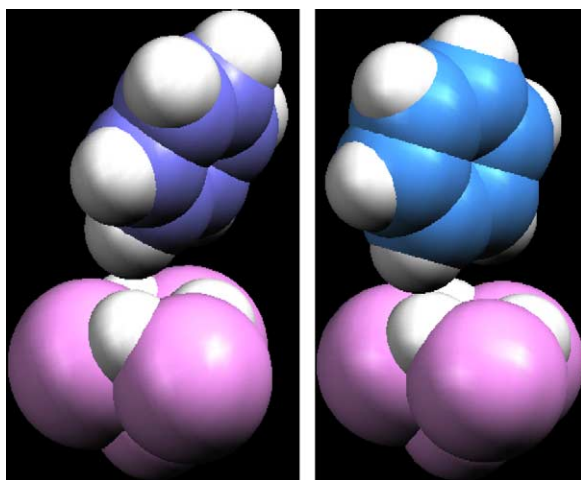


Fig. 6. Space filling representation of the host-guest complexes $[\text{C}_6\text{H}_6 \subset 3]^+$ and $[\text{C}_6\text{H}_6 \subset 4]^+$ with the benzene guest (top) approaching the Ru_3 plane, the arene ligands being omitted for clarity.

3. Conclusions

By checking the chemistry underlying the concept of “supramolecular cluster catalysis” we identified two major errors in our publications related to this topic [11–13,36], which are essentially due to contamination problems.

(1) The conversion of the “closed” cluster cation $[\text{H}_3\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})]^+$ (**1**) into the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), which we had ascribed to a reaction with water in the presence of ethylbenzene [11–13,36], is simply an oxidation reaction which occurs in the presence of air.

(2) The higher catalytic activity observed with ethylbenzene, which we had erroneously attributed to the “open” cluster cation $[\text{H}_2\text{Ru}_3(\text{C}_6\text{H}_6)(\text{C}_6\text{Me}_6)_2(\text{O})(\text{OH})]^+$ (**2**), was due to the formation of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$, caused by a hydroperoxide contamination present in ethylbenzene.

Additionally, we have been able to isolate and unequivocally characterise by X-ray crystallography the novel benzene host-guest complexes $[\text{C}_6\text{H}_6 \subset 3]^+$ and $[\text{C}_6\text{H}_6 \subset 4]^+$.

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