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Supramolecular Cluster Catalysis: Benzene Hydrogenation Catalyzed by a Cationic Triruthenium Cluster under Biphasic Conditions**

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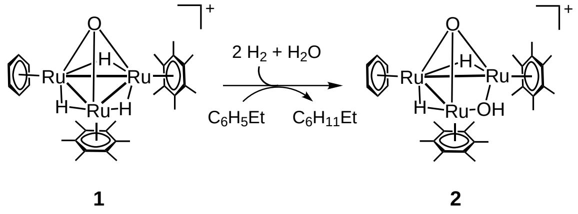
Thomas R. Ward

Dedicated to Professor Lord Lewis of Newnham

Organometallic catalysis most often proceeds 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 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 characterization 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]

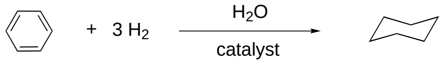
In all these reactions, the elementary steps of the catalytic process are believed to occur within the first coordination sphere of the organometallic catalyst.[5] We now have reasons to believe that organometallic catalysts may transform a substrate without prior coordination, the interactions between both partners entirely relying on weak intermolecular contacts. Although hydrogen transfer from a catalyst molecule to a substrate via a merely hydrogen-bonded catalyst–substrate complex has already been considered as the mechanism of ketone transfer hydrogenation reactions,[6] catalytic transformations by host–guest interactions and molecular recognition are generally accepted only in enzymatic catalysis.[7]

The water-soluble organometallic cluster cation **1** (see Scheme 1), accessible from $[(\eta^6\text{-}C_6H_6)Ru(H_2O)_3]^{2+}$ with $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)_3]^+$ in aqueous solution and isolated as the BF_4^- salt,[8] was found to catalyze the hydrogenation of aromatic substrates under biphasic conditions. An unusually high catalytic activity of **1** was observed for the hydrogenation of ethylbenzene. From the reaction mixture the cluster cation **2** could be isolated as the BF_4^- salt (Scheme 1).[9]



Scheme 1. Hydrolyis of the closed cluster cation **1** to give the open cluster cation **2** during the hydrogenation of ethylbenzene to ethylcyclohexane under biphasic conditions (no free C_6H_{12} or C_6Me_6 detected).

Cation **2**, dissolved in water, catalyzes the hydrogenation of aromatic compounds with higher activity than cation **1**: The reaction proceeds with a catalyst/substrate ratio of 1/1000 under hydrogen pressure (60 bar) at 110 °C with vigorous stirring of the biphasic system. For benzene, the reaction is almost complete within 15 min, the catalytic turnover number (TON) being 911, corresponding to a catalytic turnover frequency (TOF) of 3644 h^{-1}. Cation **2** can be recovered unaltered as the BF_4^- salt after a catalytic run from the aqueous phase and reused. Under identical conditions, cation **1** catalyzes the hydrogenation of benzene with a TOF of 289 h^{-1} (Scheme 2).



Scheme 2. Hydrogenation of benzene to cyclohexane catalyzed by **1**-BF_4 or by **2**-BF_4 (catalyst/substrate 1:1000, 60 bar H_2, 110 °C) in water (TOF 289 h^{-1} for **1** and 3544 h^{-1} for **2**, respectively).

Although a large number of organometallic complexes are known to catalyze the hydrogenation of olefins or acetylenes, only very few complexes are reported to catalyze the hydrogenation of aromatic compounds (TOF given in parantheses): $[(\eta^6\text{-}C_6Me_6)_2Ru_2(\mu_2\text{-}H)(\mu_2\text{-}Cl)_2]Cl_2$ (241 h^{-1}),[10] $[(\eta^5\text{-}C_5Me_5)_2Rh_2(\mu_2\text{-}Cl)_2]$ (11 h^{-1}),[11] $[(\eta^3\text{-}C_3H_5)Co(P(OMe)_3)_3]$ (0.7 h^{-1}),[12] $[RuH_2(\eta^2\text{-}H_2)_2(PCy_3)_2]$ (1.6 h^{-1}),[13] $[Nb(OC_6HPh_4\text{-}2,3,5,6)_2Cl_3]$ in combination (1:3) with BuLi (409 h^{-1}),[14] $[(\eta^6\text{-}C_6H_6)_4Ru_4(\mu_3\text{-}H)_4]Cl_2$ in water (376 h^{-1})[15] or in ionic liquids (364 h^{-1}),[16] and $[(\eta^6\text{-}C_6H_6)_2Ru_2(\mu_2\text{-}Cl_2)Cl_2]$ (1998 h^{-1}) in water.[17] The hydrogenation of arenes falls in general within the domain of heterogeneous catalysis: Millions of tons of benzene are hydrogenated per year to give cyclohexane using Raney nickel as the heterogeneous catalyst; the so-called IFP (Institut Français du Petrole) process[18] using nickel and cobalt salts in combination with triethylaluminum seems destined to take over.[19]

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In the case of **2**, catalyzing the hydrogenation of ethylbenzene, no substitution of a η^6-bonded arene ligand (benzene or hexamethylbenzene) in **2** by ethylbenzene is observed. The recovered material shows the identical ^1H NMR spectrum and the same catalytic activity for further catalytic runs as the original **2**-BF_4. This striking observation rules out the conventional organometallic mechanism for the catalytic hydrogenation of aromatic substrates by **2**, in which the substrate is coordinated to the metal of the active complex, because in this case one of the three arene ligands (either benzene or hexamethylbenzene) in **2** should be replaced by ethylbenzene. We therefore conclude that the aromatic substrate molecule is not coordinated to ruthenium throughout the catalytic cycle but interacts with the Ru_3 surface in **2** only through weak intermolecular interactions. This may be possible thanks to the three η^6-arene ligands in **2** which form a hydrophobic pocket capable of accommodating the aromatic substrate and in placing it in a perfect position underneath the Ru_3 face opposite to the oxo cap of the cluster. In the spirit of the triterpene cyclases[7] and due to the lipophilic character of both substrate and catalyst binding pocket, the host–guest interaction is very favorable, as the aromatic substrate tries to escape from the aqueous medium.

To verify this hypothesis, we carried out a mass spectrometric study of mixtures of hexadeuterobenzene with **1** and with **2** (as BF_4^- salts) in acetone. The adducts $C_6D_6 \subset \mathbf{1}$ and $C_6D_6 \subset \mathbf{2} \cdot H_2O$ can be clearly identified in the electrospray mass spectrum. The intensity of these peaks, which can be assigned unambiguously on the basis of their characteristic Ru_3 isotope pattern, increases with the concentration of C_6D_6 in the acetone solution. These results strongly support the hypothesis of host–guest interactions between the substrate and the catalyst.

Facial coordination of an arene on the triangular face of a cluster has been known since the characterization of $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ by Lewis et al.[20] These structures have been invoked as models for the chemisorption of arene derivatives at a threefold site of close-packed metal surfaces. Incorporating arene derivatives as ancillary ligands constitutes a good model for the interaction between a hydrophobic triangular face and an arene derivative. A search of the Cambridge Structural Database reveals eleven such structures composed of three $\{(\eta^5\text{-}C_5R_5)M\}$ moieties capped by an arene, yielding $[(\eta^5\text{-}C_5R_5)_3M_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})]^{n+}$ (M = Co, Ru, Rh, R = H, Me; Figure 1 a).[21] Comparing these structures to the molecular structure of clusters **1** and **2** (Figure 1 b) suggests that these are preorganized to accommodate a benzene host. However, it should be emphasized that all three ruthenium centers in clusters **1** and **2** are coordinatively saturated and thus cannot interact through dative bonds with the arene host. The host–guest interaction must rely solely on weak hydrophobic and van der Waals contacts. Moreover, the bridging hydrides and hydroxide shield the access of the guest to the metal face.

In a modeling study,[22] a benzene molecule was docked in the hydrophobic pocket spanned by the three η^6-bonded arene ligands. Setting the {Ru_3face}–benzene distance at 3.00 Å and minimizing the steric repulsion suggests that no major cluster reorganization is necessary to accomodate a benzene host in the hydroxo-bridged cluster **2** (shortest H–H contact 1.60 Å; Figure 1 c). With the catalytically less active cluster **1**, a similar procedure yields shorter H–H contacts (1.28 Å) in the energy-minimized structure, suggesting that the cluster must relax to accomodate the benzene guest.

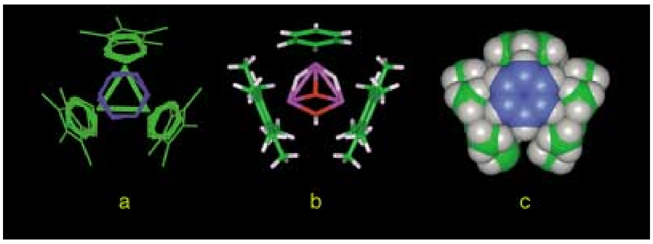
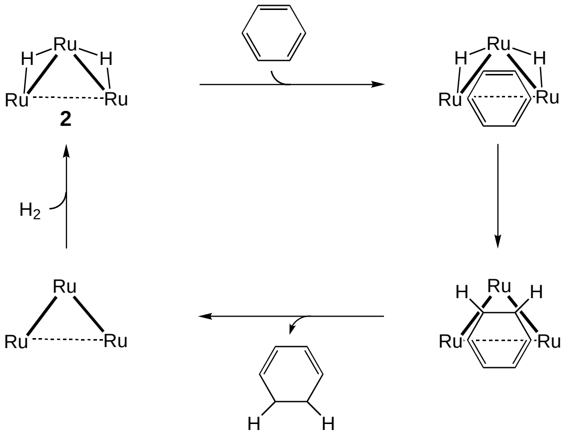


Figure 1. a) Superposition of the molecular structure of the eleven structurally characterized clusters $[(\eta^5\text{-}C_5R_5)_3M_3(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-arene})]^{n+}$ (M = Co, Ru, Rh); hydrogen atoms and arene substituents are omitted for clarity. b) Molecular structure of **2**, emphasizing the hydrophobic pocket and the preorganization to accomodate a benzene guest (compare with Figure 1 a; C: green; H: white; Ru: magenta; O: red). c) CPK model of the optimized structure of $C_6H_6 \subset \mathbf{2}$; the $\{Ru\}_3$-C_6H_6 distance fixed at 3 Å, η^6-bound arenes green and white, docked benzene blue and white.

We believe the hydrogenation of the aromatic substrate to occur within the hydrophobic pocket of the catalyst in a stepwise manner, that is to say via cyclohexadiene and cyclohexene intermediates. Thus, hydrogenation of the disubstituted *o*-, *m*-, and *p*-xylenes afford both *cis* and *trans* isomers of the corresponding dimethylcyclohexanes. This implies that after the dihydride transfer, the (partially) reduced substrate leaves the hydrophobic pocket, allowing regeneration of the active catalyst by H_2 oxidative addition. Accordingly, in the hydrogenation of benzene with **2**-BF_4 under biphasic conditions (catalyst/substrate ratio of 1/1000, H_2 60 bar, 20 °C, 1 h), small amounts of 1,3-cyclohexadiene and of cyclohexene can indeed be detected by GC analysis. A mechanism consistent with these observations is outlined in Scheme 3.

The reaction of cyclohexene with D_2 catalyzed by **2**-BF_4 in H_2O (catalyst/substrate ratio of 1/1000, D_2 40 bar, 110 °C, 15 min) affords exclusively 1,2-dideuterocyclohexane, suggesting that the hydrogenation mechanism involves indeed a



Scheme 3. Proposed mechanism for the stepwise catalytic hydrogenation of benzene to cyclohexane (first step: benzene to 1,3-cyclohxadiene) with the intact cluster cation **2** (arene, oxo, and hydroxo ligands omitted for clarity).

dihydride transfer from the cluster to the unsaturated substrate rather than a monohydride transfer from the cluster followed by protonation from water.

The hypothesis of supramolecular catalysis is further supported by the striking substrate selectivity of these cluster catalysts: Indeed, only benzene and moderately hindered benzene derivatives (such as toluene, ethylbenzene, xylenes), are efficiently hydrogenated. As can be appreciated from Figure 1c, highly substituted benzene derivatives (e.g. tetra- and hexamethylbenzene) are too bulky to fit into the hydrophobic pocket of **1** and **2** and are thus not hydrogenated.

To rule out the possibility of catalysis by microparticles (colloids or nanoclusters), we carried out a mercury poisoning experiment.[23–25] Mercury is well known to poison heterogeneous catalysts by amalgam formation; catalytically active metal particles formed by degradation of molecular precursors will therefore be amalgamated, which causes a complete loss of the catalytic activity.[26] A solution of **2**-BF_4 in water, however, stirred with metallic mercury for 1 h prior to filtration, shows almost the same catalytic activity for benzene hydrogenation as before (TOF 3500 h^{-1}). This experiment clearly suggests that intact Ru_3 clusters are the catalytically active species.

With **2**-BF_4 as the catalyst, benzene can even be hydrogenated at room temperature: Under biphasic conditions (water/benzene) and a hydrogen pressure of 60 bar, the conversion of benzene is 98% after 4 h (TON 980, TOF 245 h^{-1}). No other catalyst is known to hydrogenate benzene under such mild conditions.

From an academic point of view, arene hydrogenation catalysts **1** and **2** are of interest as they seem to pave the way towards a shift in paradigm for cluster catalysis. Indeed, clusters are often regarded as molecular architectures that lie at the interface between homogeneous and heterogeneous systems. The catalytic systems described herein lie at the interface between homogeneous, heterogeneous, and enzymatic catalysis. From an industrial point of view, catalyst **2** may be of great interest as it is, to the best of our knowledge, the mildest and most efficient molecular arene hydrogenation catalyst reported to date. Furthermore, these catalysts are devoid of expensive ligands: they can be formally regarded as solubilized ruthenium ions, the ligands provided either by the solvents (arene or water-derived anions) or the gas (H_2).

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