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

Georg Süß-Fink,* Matthieu Faure, and Thomas R. Ward

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 carbylonylation 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 [(η⁵-C₅H₅)Ru(H₂O)]⁺ with [(η⁶-C₅Me₅)Ru(μ-H)]²⁺ in aqueous solution and isolated as the BF₄⁻ 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 BF₄⁻ salt (Scheme 1).[9]

Scheme 1. Hydrolysis 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 C₆H₆; or C₅Me₅ 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 BF₄⁻ 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-BF₄ or by 2-BF₄ (catalyst/substrate: 1:1000, 60 bar H₂, 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): [(η⁵-C₅Me₅)RuH₂(μ-H)(μ-Cl)]₂Cl (241 h⁻¹)[10] [(η⁵-C₅Me₅)Rh₂(μ-Cl)] (11 h⁻¹)[11] [(η⁶-C₅H₅)Co(P(OMe)₃)]₂ (0.7 h⁻¹)[12] [RuH₂(η²-H₃)(PCy₃)]₂ (1.6 h⁻¹)[13] [Nb(OC₆H₄-HPc₂-2,3,5,6)Cl₃] in combination (1:3) with BuLi (409 h⁻¹)[14] [(η⁶-C₅H₅)Ru₂(μ-H)]Cl₂ in water (376 h⁻¹)[15] or in ionic liquids (364 h⁻¹)[16] and [(η⁵-C₅H₅)Ru₂(μ-Cl)]Cl₂ (198 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 triethylalumimum seems destined to take over.[19]

[1] Prof. Dr. G. Süß-Fink, M. Faure, Prof. Dr. T. R. Ward
Institut de Chimie, Université de Neuchâtel
Case postale 2, 2007 Neuchâtel (Switzerland)
Fax: (+ 41) 32-718-2511
E-mail: georg.suess-fink@unine.ch

[2] This work was supported by the Fonds National Suisse de la Recherche Scientifique. A generous loan of ruthenium chloride by the Johnson Matthey Technology Centre is gratefully acknowledged.
In the case of 2, catalyzing the hydrogenation of ethylbenzene, no substitution of a η²-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-BF₃. 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 Ru₃ face in 2 only through weak intermolecular interactions. This may be possible thanks to the three η²-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 Ru₃ face opposite to the oxo cap of the cluster. In the spirit of the triterpene cyclases[23] 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 BF₃-salts) in acetone. The adducts C₆D₆⊂I and C₆D₆⊂2-H₂O 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 Ru₃ isotopic pattern, increases with the concentration of C₆D₆ 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 [Os₂-(CO)₆(μ₂-η²:η²:C₆H₆)] by Lewis et al.[24] 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 [(η²-C₆R₆)Ru₃] moieties capped by an arene, yielding [(η²-C₆R₆)Ru₃(μ₂-η²:η²:η²-C₆H₆)]⁹⁺ (M = Co, Ru, Rh, R = H, Me; Figure 1a).[21] Comparing these structures to the molecular structure of clusters 1 and 2 (Figure 1b) 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 η²-bonded arene ligands. Setting the [Ru₃face]–benzene distance at 3.00 Å and minimizing the steric repulsion suggests that no major cluster reorganization is necessary to accommodate a benzene host in the hydroxy-bridged cluster 2 (shortest H–H contact 1.60 Å; Figure 1c). 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 accommodate the benzene guest.

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-xylene affords both cis and trans isomers of the corresponding dimethyleneoxohexanes. This implies that after the dihydride transfer, the (partially) reduced substrate leaves the hydrophobic pocket, allowing regeneration of the active catalyst by H₂ oxidative addition. Accordingly, in the hydrogenation of benzene with 2-BF₃ under biphasic conditions (catalyst/substrate ratio of 1/1000, H₂ 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 D₃ catalyzed by 2-BF₃ in H₂O (catalyst/substrate ratio of 1/1000, D₂ 40 bar, 110°C, 15 min) affords exclusively 1,2-dideuterocyclohexane, suggesting that the hydrogenation mechanism involves indeed a
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, xylene), 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 amalagamation; 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-BF₄ in water, however, stirred with metallic mercury for 1 h prior to filtration, shows almost the same catalytic activity for benzene hydrogenation as before (TON 3500 h⁻¹). This experiment clearly suggests that intact Ru₃ clusters are the catalytically active species.

With 2-BF₄ 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 enzyme-like 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 (H₂).

Received: July 5, 2001 [Z.17456]