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Homogeneous Catalysis by Metal Clusters. 2.[†] Tetranuclear Osmium Complexes as Catalyst Precursors in the Hydrogenation of Styrene

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The hydrogenation of styrene is efficiently catalyzed by $H_3Os_4(CO)_{12}(I)$ (**1**), $H_4Os_4(CO)_{12}$ (**2**), $[H_2Os_4(CO)_{12}(I)]^-$ (**3**), and $[H_3Os_4(CO)_{12}]^-$ (**4**) in decalin solution at 140 °C and 800 Torr of H_2. The homogeneity of the reaction was established by a combination of chemical tests. The reaction rate is dependent on the structure of the cluster and is first order with respect to the concentrations of styrene and hydrogen; the turnover frequency, however, increases with decreasing cluster concentration. These results, together with the observed influence of added CO and other relevant data, are interpreted in terms of cluster fragmentation to yield low concentrations of highly active species of lower nuclearity. This type of fragmentation is proposed as a general phenomenon for reactions catalyzed by simple metal carbonyl clusters.

Homogeneous catalysis by metal clusters has been a subject of much interest in recent years, mainly because it may serve as a model for heterogeneous reactions and because it may lead to multiple-metal-site reactivities unknown for mononuclear complexes.[1,2]

A prerequisite for such concepts to be valid is that the polynuclear metal framework must remain intact during the catalytic cycle or at least that mononuclear complexes or metallic particles are not responsible for the catalytic activity. Therefore, a good proportion of the published work has been aimed at establishing the participation of a cluster in the catalytic reaction mechanism; this question, however, still remains essentially open.

To our knowledge, there are no reports of a homogeneous reaction that is *catalyzed* by a metal cluster but not by mononuclear complexes. Although spectroscopic and reactivity studies have provided very interesting evidence for cluster catalysis,[3] these data have been generally obtained under noncatalytic conditions, and it is always possible that undetectable amounts of mononuclear species or metallic particles are responsible for the observed activity under real working conditions. This is also true with respect to the recovery of high yields of the starting cluster after a catalytic run as evidence for cluster participation in the cycle.[4–6] Kinetic measurements are also a powerful tool for the study of cluster catalysis, but the systems are generally complex and consequently often yield results of difficult or ambiguous interpretation.[7–9]

A simple reaction, adequate for detailed studies, is the hydrogenation of alkenes, which has been achieved for polynuclear complexes of Ru,[10–16], Os,[17–19] Rh,[20] Ni,[21] Pt,[22] and mixed metals.[4] We have recently been involved in synthetic and catalytic studies using polynuclear osmium carbonyl complexes.[23] Continuing this line of research, we now describe an investigation of the homogeneous hydrogenation of sytrene by tetranuclear osmium clusters; kinetic and other data are discussed in relation to the question of cluster integrity during the catalytic cycle.

Results and Discussion

The hydrogenation of styrene to ethylbenzene in decalin solution is efficiently catalyzed by the tetranuclear osmium complexes **1–4** listed in Table I; this is a very clean reaction that may be carried out at ambient or subambient pressure, thus allowing continuous and accurate rate measurements. Moreover, complexes **1–4** are known to be thermally and oxidatively highly stable, thus reducing the probability of facile fragmentation processes taking place under the experimental conditions.

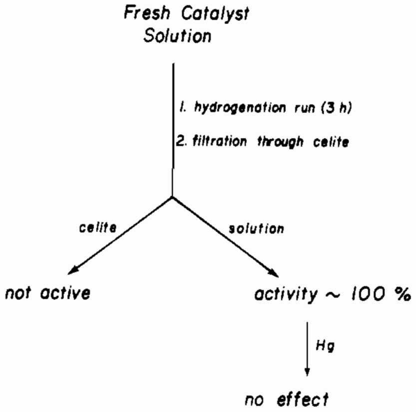
Typical reaction behavior as a function of time for the four catalyst precursors is shown in Figure 1; it is interesting to note that the activity of the butterfly-shaped cluster **1** is considerably higher than those observed for the tetrahedral species **2–4**. This would be expected to be the case if the integrity of the clusters is maintained during the catalysis, since a butterfly metal framework is electronically less saturated than a tetrahedral arrangement. An alternative explanation, which we now favor (vide infra), is that the butterfly species **1** is more easily fragmented than the tetrahedral complexes **2–4**.

Table I. Hydrogenation of Styrene by Tetranuclear Osmium Clusters[a]

catalyst	r_i[b]	10^3k_{obsd}[c]
$H_3Os_4(CO)_{12}(I)$ (**1**)	583 ± 2	22.7 ± 0.2
$H_4Os_4(CO)_{12}$ (**2**)	87 ± 2	5.1 ± 0.1
$[H_2Os_4(CO)_{12}(I)]^-$ (**3**)	63 ± 2	2.07 ± 0.03
$[H_3Os_4(CO)_{12}]^-$ (**4**)	52.0 ± 0.0	1.96 ± 0.00

[a] Conditions: 140 °C; 800 torr of H_2; [styrene] = 1.2 M; [catalyst] = 1.12×10^{-4} M; **3** and **4** are used as $[N(PPh_3)_2]^-$ salts. [b] r_i in mmol of H_2 consumed (mmol of cluster)$^{-1}$ h^{-1}. [c] k_{obsd} in M^{-1} h^{-1}.

Scheme I. Homogeneity Tests for Styrene Hydrogenation Catalyzed by Osmium Complexes



[†] For part 1 see ref 23a.

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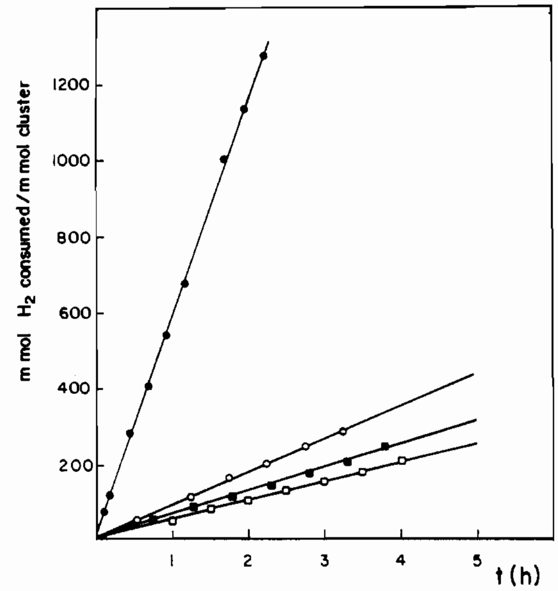

Figure 1. Hydrogenation of styrene catalyzed by tetranuclear osmium clusters (conditions as in Table I): (●) **1**; (○) **2**; (■) **3**; (□) **4**.

Homogeneity Tests. A question that is seldom addressed but that is of prime importance in establishing the nature of the active species, particularly in hydrogenation reactions, is the possibility that very small amounts of highly active metallic particles are responsible for the observed catalysis.

Visual homogeneity of the solution, although indicative, is by no means conclusive evidence for the absence of suspended or colloidal metal. Several tests have been suggested in the literature for establishing the homogeneous nature of a catalytic reaction.[24,25]

We have used a combination of methods to study this problem in our reactions: (i) The first procedure, summarized in Scheme I, combines techniques separately described by Maitlis[24] and Crabtree[25] and does not require any special equipment or reagents; furthermore, the whole test is conducted under catalytic conditions, as follows. A fresh catalyst solution is used in a 3-h hydrogenation run; the solution is then filtered through Celite under Ar in order to retain any metal particles in the filter. Hydrogenation runs were then carried out under the same conditions, using as catalysts the Celite filter and the filtered solution. No catalytic activity was observed for the Celite, whereas the used solution retained ca. 100% of its catalytic activity. In order to further test for colloidal metal that may pass through the filter, the activity of the used solution is again measured in the presence of liquid Hg, which is known to deactivate metallic catalysts but not homogeneous systems. No effect of Hg on the catalysis was observed. (ii) As an independent confirmation of the homogeneity of the reaction, the complex $OsCl_2(Me_2SO)_4$[26] is treated with H_2 in decalin at 150 °C for 48 h, after which it has been extensively decomposed to metallic osmium; styrene is added at this point and a hydrogenation run is carried out. The activity of the osmium metal generated in this way corresponds to less than 10% of the activity found for the cluster solutions.

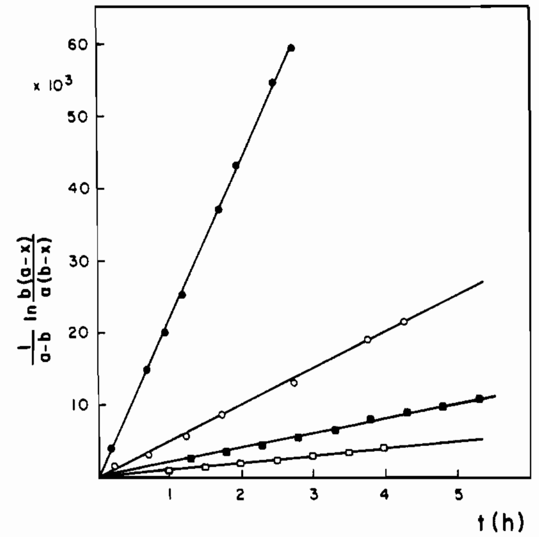

Figure 2. Integrated rate expression for the hydrogenation of styrene catalyzed by osmium clusters (conditions as in Table I): (●) **1**; (○) **2**; (■) **3**; (□) **4**.

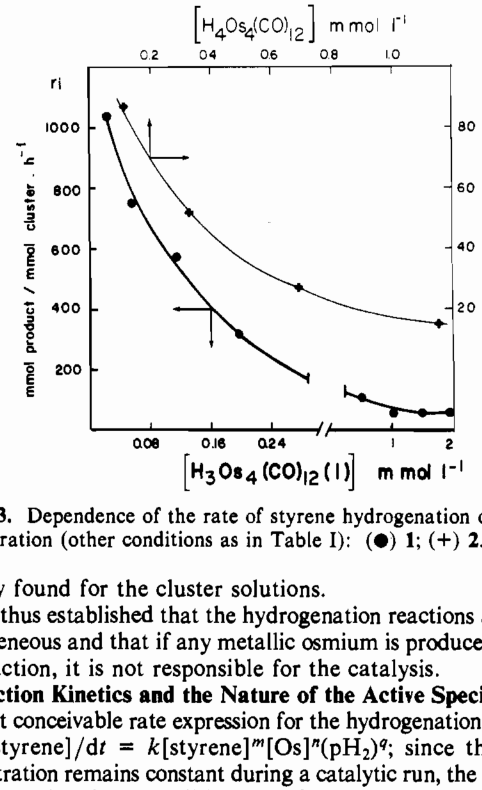

Figure 3. Dependence of the rate of styrene hydrogenation on cluster concentration (other conditions as in Table I): (●) **1**; (+) **2**.

It is thus established that the hydrogenation reactions *are* truly homogeneous and that if any metallic osmium is produced during the reaction, it is not responsible for the catalysis.

Reaction Kinetics and the Nature of the Active Species. The simplest conceivable rate expression for the hydrogenation reaction is $-d[\text{styrene}]/dt = k[\text{styrene}]^m[\text{Os}]^n(pH_2)^q$; since the metal concentration remains constant during a catalytic run, the observed kinetics under these conditions are further reduced to $-d[\text{styrene}]/dt = k_{obsd}[\text{styrene}]^m(pH_2)^q$. For $m = q = 1$ the integrated form is $(1/a - b) \ln [b(a - x)] = k_{obsd}t$, where a and b are the initial concentrations of H_2 and styrene and x is the amount of H_2 or styrene consumed at time t (further details in the Experimental Section). Plots of the left side of this equation against t are linear (Figure 2) and yield the values of k_{obsd} collected in Table I. Thus, the hydrogenation reaction is first order with respect to both styrene and hydrogen concentrations.

However, the rate dependence on other reaction parameters, which are kept constant during each catalytic run, is more complex. The variarion of the rate with *cluster* concentration has been used as a method for studying the nature of the active species in cases where cluster catalysis has been suspected.[9,15,27] As shown in Figure 3, the variation of the rate of styrene hydrogenation

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catalyzed by clusters **1** and **2** is obviously nonlinear; the turnover frequency *increases* with decreasing cluster concentration, indicating that the hydrogenation rate is not first order with respect to *cluster* concentration. We have not found any simple reasonable mathematical correlation between these data and an approximate rate order. This is in contrast with the results reported by Doi et al. for ethylene hydrogenation catalyzed by $H_4Ru_4(CO)_{12}$,[15] which is to our knowledge the only case for which a first-order rate dependence on cluster concentration has been observed. We note, however, that in Doi's work kinetic data were measured by syringing out samples of the gases *above* the solution and analyzing very small amounts of ethane by GLC. Furthermore, the hydrogenation rates measured in this way were insensitive to stirring of the solution, whereas we have noted in our case that rapid stirring without vortexing is important in ensuring reproducibility of the results (see Experimental Section). It is possible that the concentrations of gaseous products measured by Doi are not representative of the composition of the system as a whole, since the liquid phase including the very soluble hydrocarbon gases is ignored in the measurements. We believe that manometric measurement of the hydrogen uptake is a more direct and accurate manner of following this type of reaction.

Results similar to ours have been described for the hydrogenation of benzaldehyde catalyzed by $Rh_6(CO)_{16}$[7] and for the $Ru_3(CO)_{12}$-catalyzed water-gas shift reaction[27] and interpreted in terms of cluster fragmentation.

Although we have not found a simple mathematical expression for which a linear plot of our data is obtained, these results may be interpreted in terms of two possible processes: (i) fragmentation of inactive Os_4 clusters into highly active species of *lower* nuclearity (eq 1), which would be favored at low cluster concentrations, or (ii) aggregation of active Os_4 clusters into inactive species of ***higher*** nuclearity (eq 2), which would be favored at high catalyst concentrations.

$$Os_4 \text{ (inactive)} \rightarrow Os_{<4} \text{ (active)} \qquad (1)$$

$$Os_4 \text{ (active)} \rightarrow Os_{>4} \text{ (inactive)} \qquad (2)$$

We prefer the fragmentation rather than the aggregation hypothesis on the following grounds: (i) IR spectra of the solutions after the catalytic runs are essentially identical with those of the starting clusters. This is consistent with the tetraosmium complex acting as a *source* of highly active fragments of lower nuclearity, probably produced in very low concentration, whose IR spectra are undetectable or are masked by those of the unmodified parent clusters. On the other hand, if the aggregation process is invoked, it is required that a large proportion of the osmium be transformed into the inactive higher nuclearity species in order for an overall deactivation effect to be observable at high catalyst concentrations; if this were the case, the IR spectrum of the aggregated form should be dominant, or at least observable, after the catalytic run, which is not in accord with the experimental facts. (ii) When **1** and **2** are supported on MgO, stable surface-bound clusters are formed.[28] These species are inactive for the hydrogenation of styrene under reaction conditions for which the supported clusters are apparently unmodified; i.e., the support seems to stabilize the complexes toward fragmentation and thereby inhibits the catalytic activity. (iii) We have previously demonstrated that mononuclear osmium complexes are highly active catalysts in the hydrogenation of alkenes and other related reactions;[29] the compound $OsHCl(CO)(PPh_3)_3$ also hydrogenated styrene efficiently. In fact, when a concentration of this mononuclear catalyst precursor corresponding to ca. 10% of the concentration of the clusters was used, a turnover frequency of 615 ± 34 mmol of product (mmol of catalyst)$^{-1}$ h^{-1} was measured. This result is comparable to those obtained in the reaction catalyzed by **1** and consistent with the proposed fragmentation process. (iv) We have tested the complex $Co_4(CO)_9[HC(PPh_2)_3]$, which is known to be resistant to fragmentation,[30,31] and have found it inactive in the hydrogenation of styrene. The complex is also inactive in the hydroformylation of hex-1-ene under reaction conditions for which no fragmentation is observed and becomes active at high temperatures and pressures under which the formation of $Co_2(CO)_8$ is easily detected by IR spectroscopy, i.e. under conditions for which fragmentation takes place. Similar observations were reported by Vahrenkamp for styrene hydrogenation catalyzed by ligand-stabilized heteronuclear clusters.[4]

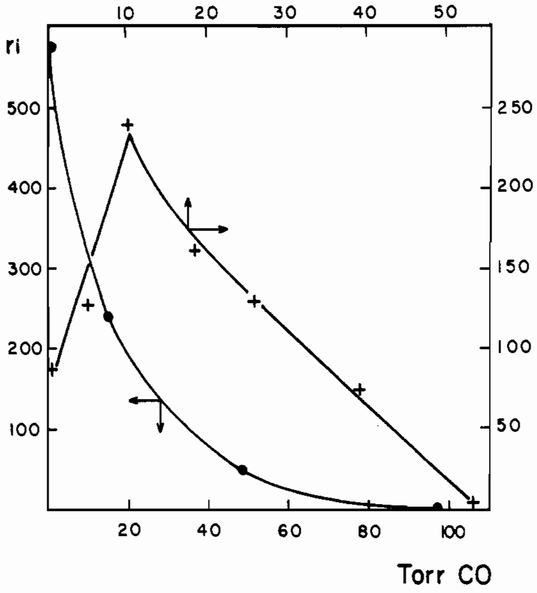

Figure 4. Influence of added CO on the rate of styrene hydrogenation (other conditions as in Table I): (●) **1**; (+) **2**.

The effect of added CO on the hydrogenation of styrene catalyzed by **1** and **2** is shown in Figure 4. For **1**, a strong inhibition of the hydrogenation rate by CO is observed, whereas for **2** a promoting effect is observed at low CO pressures (up to 10 Torr) and strong inhibition occurs at higher pressures. These results are similar to those of other reported cases,[4,8] but their interpretation is not straightforward, since added CO might stabilize the cluster or might favor metal–metal bond rupture, depending on the starting material and the reaction conditions. Moreover, CO may effectively compete with the olefin for the active species once it has been formed, and thus the measured effect could be a superposition of two or more independent processes.

Conclusions. We have demonstrated that tetranuclear osmium clusters are efficient catalyst precursors for the hydrogenation of styrene under moderate reaction conditions.

There is no participation of metallic osmium in the catalysis.

Although our data do not allow us to establish the identity of the active species or the detailed rate expression for the reaction, kinetic, spectroscopic, and other evidence indicates that the tetranuclear osmium clusters are *not* directly involved in the catalytic cycle but most probably undergo fragmentation to produce low concentrations of lower nuclearity (perhaps mononuclear) species responsible for the observed activity.

Considering that hydrogenation of terminal alkenes is a rather facile reaction and that Os–Os bonds are among the strongest in metal clusters, we believe that fragmentation may be a general process and thus it may be difficult to find simple carbonyl clusters that are catalytically active and simultaneously resist fragmentation reactions. A delicate balance between metal–ligand and metal–metal bond strength has to be attained in order to achieve cluster catalysis. This points toward the use of nonclassical ligands such as macromolecules or inorganic oxides, and we are currently directing our research efforts in these directions.

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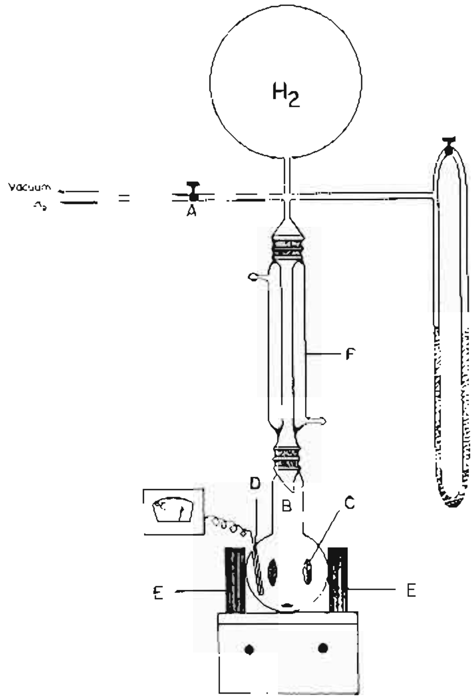

Figure 5. Hydrogenation apparatus.

Experimental Section

Materials. The complexes 1–4,[32] $OsHCl(CO)(PPh_3)_3$,[26] and $Co_4(CO)_9[HC(PPh_2)_3]$[30] were prepared by published procedures. Styrene (Aldrich) was dried over $CaCl_2$, passed through an alumina column, and distilled under reduced pressure before use. Hydrogen was purified by passage through a series of columns containing CuO/Al_2O_3, molecular sieves (3A), and $CaCl_2$. Solvents were distilled under N_2 over appropriate drying agents.

Apparatus and Procedure. The system used for the hydrogenation experiments is schematically shown in Figure 5. Stopcock A connects the apparatus to a high-vacuum line and to the source of purified hydrogen. The glass reactor B is a 100-mL round-bottom flask with four vertical indentations C and a thermowell D; this allows direct measurements of the *solution* temperature and rapid stirring without vortex formation, which is of prime importance in ensuring reproducibility of the results. The reaction is heated by means of an electric oven E, which may be controlled to ±0.5 °C and is further connected to a condenser F kept at 0 °C by means of a cryostat in order to avoid styrene vapor escaping from the solution into the hydrogen reservoir. The total volume of the system is ca. 2 L.

In a typical experiment a solution of the catalyst (4.5×10^{-3} mmol) and the olefin (52 mmol) in decalin (35 mL) was placed in the reactor B, which was then sealed to the condenser F by use of Apiezon wax. The solution was carefully deoxygenated by three freeze–pump–thaw cycles; hydrogen was then admitted into the evacuated system to the desired pressure. Subsequently, the preheated oven was placed around the reactor and magnetic stirring was immediately commenced. The reaction was followed by measuring hydrogen pressure as a function of time. At the end of the run the composition of the solution was analyzed by means of a Varian 3700 gas chromatograph fitted with a flame ionization detector and a 3-m 10% SP-2100 on Supelcoport stainless steel column; the chromatograph was coupled with a Varian Vista 401 automatic data system. Final conversions measured in this way were essentially identical with those calculated from pressure data; ethylbenzene was the only product detected. Each reaction was repeated at least three times in order to ensure reproducibility of the results; data reported in Table I thus represent average values for each complex.

Calculations. The measured pH_2 values were first converted to millimoles of H_2 consumed; in order to compare the various catalysts, the data were plotted as turnovers (mmol of H_2 consumed/mmol of cluster) vs. t, yielding straight lines as shown in Figure 1. Initial hydrogenation rates r_i in turnover frequency units were then obtained from the corresponding slopes. Values of k_{obsd} were similarly obtained from the slopes of the linear plots corresponding to the integrated second-order rate expressions shown in Figure 2. For these plots the initial concentration of hydrogen, a, is taken as the total number of moles of H_2 admitted into the system divided by the total volume; the molar fraction of hydrogen *in the solution* under our reaction conditions is very small (ca. 3×10^{-4}).[33] Since the design of the reactor and the experiments were conceived to avoid diffusion effects, we may assume that this concentration of dissolved hydrogen remains constant during a catalytic run by rapid equilibration from the gas phase as the dissolved gas is consumed in the reaction. Therefore, what is actually *measured* is the change in the total concentration of hydrogen in the system, which in turn represents the rate at which the olefin is being hydrogenated. All the straight lines were fitted by conventional linear regression programs $r > 0.998$.

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[32] Complexes 1–3 were prepared as described in: Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356. Complex 4 was synthesized according to ref 23b.

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