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HYDROGENATION OF PENTYNES WITH $Rh_4(CO)_{12}$ AND $Rh_2(CO)_4Cl_2$ IN SOLUTION AND ANCHORED ON Al_2O_3

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Summary

The catalytic activities of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ for the homogeneous hydrogenation of pentynes in toluene have been studied and compared with those of these complexes anchored on γ-Al_2O_3. $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ interact strongly with γ-Al_2O_3, and the resulting species give identical IR spectra in the C—O stretching region characterised by absorptions at 2080 cm^{-1} and 1997 cm^{-1}, suggesting that the same carbonylrhodium active centres are formed upon binding of both metal carbonyls. However, $Rh_4(CO)_{12}/Al_2O_3$ and $Rh_2(CO)_4Cl_2/Al_2O_3$ show completely different behaviour as catalysts in the hydrogenation of pentynes; $Rh_2(CO)_4Cl_2/Al_2O_3$ is more active than $Rh_2(CO)_4Cl_2$ in solution, while the activity of $Rh_4(CO)_{12}$ is not substantially altered upon going from the homogeneous to the heterogenised system.

Complete hydrogenation to give pentane is favored when $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ are bound to Al_2O_3, and occurs much more slowly when the complexes are used as homogeneous catalysts.

Introduction

Transition metal clusters have found several applications in the last few years. Not only have they been considered as simplified models of metal surfaces for chemisorption and catalysis [1,2], but they have also been used as a source of highly dispersed metallic catalysts when decomposed on metal oxides [3—5]. There is, moreover, a rapidly growing literature on cluster compounds bound to polymeric or inorganic supports [6,7], which are believed to combine the advantages of homogeneous catalysts, such as efficiency and selectivity, with those of heterogeneous catalysts such as easy separation of the products

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and recovery of the catalyst. Stabilisation of the cluster compound on the support has also been claimed in some cases [8,9]. Most of the studies in this field are concerned with an investigation, by IR techniques, of the modifications undergone by the cluster compound as a result of its attachment to the support under various experimental conditions [10—13] and with the evaluation of its catalytic activity in specific reactions [14—16]. However, there has been little systematic investigation of the behaviour of these heterogenised catalysts.

The present study was intended to investigate the performance of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ bound to γ-Al_2O_3 as catalysts for the hydrogenation of 2-pentyne and 1-pentyne, and to compare their behaviour with that of toluene solutions of the same carbonyl compounds. No attempt was made to characterise at the molecular level the active species formed on the support and during the reaction, neither was the Al_2O_3 subjected to drastic thermal treatments which limit the utilisation of any catalytic system for practical purposes.

Results

Absorption of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ on Al_2O_3

When a toluene solution of $Rh_4(CO)_{12}$ is left in contact with alumina at room temperature under vacuum, the oxide acquires a brown colour while the solution lightens and is completely discoloured within one hour. Removal of the solvent under vacuum causes the colour of alumina to turn initially violet and then, after longer pumping periods, beige. The IR spectrum of a sample of $Rh_4(CO)_{12}$ anchored on Al_2O_3, taken at this stage, is shown in Fig. 1a. Two absorption bands are present in the terminal carbonyl stretching region at 2080 cm^{-1} and at 1997 cm^{-1}. No absorptions were observed in the bridge C—O stretching region, either because they were not present, were too weak, or were covered by the Al_2O_3 absorption.

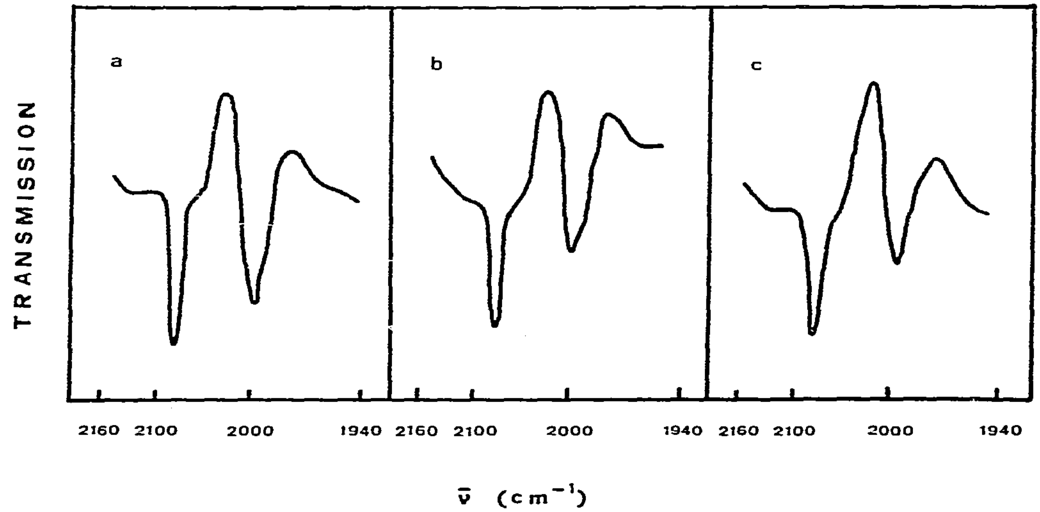

Fig. 1. Infrared spectra in the terminal C—O stretching region of $Rh_4(CO)_{12}$ (a), $Rh_2(CO)_4Cl_2$ (b) and $Rh_6(CO)_{16}$ (c) bound to γ-Al_2O_3.

$Rh_2(CO)_4Cl_2$ is taken up by Al_2O_3 more rapidly than is $Rh_4(CO)_{12}$, and the process is complete in less than 20 minutes. The alumina at this stage has a yellowish colour, and this turns to dark grey upon standing. Removal of solvent causes the alumina to become violet and then beige as observed for $Rh_4(CO)_{12}$ on Al_2O_3. An IR spectrum of $Rh_2(CO)_4Cl_2$ absorbed on Al_2O_3 is shown in Fig. 1b and is identical with that of $Rh_4(CO)_{12}$ anchored on Al_2O_3.

The same IR bands are obtained also from $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ bound to basic or acidic Al_2O_3.

A spectrum taken under the same experimental conditions for a sample of $Rh_6(CO)_{16}$ adsorbed on Al_2O_3 is shown in Fig. 1c.

Both $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ appear to be strongly bound to the Al_2O_3 surface and cannot be extracted into toluene under 1 atm CO at 80° C.

Heating of $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ on Al_2O_3 at 80° C for 1 h under 1 atm of H_2 does not cause any change in the position and/or the number of IR absorptions in the C—O stretching region.

Hydrogenation experiments

$Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ catalyse the hydrogenation of 2-pentyne and 1-pentyne both in solution and when bound to γ-Al_2O_3. The hydrogenation takes place also at low temperature (30° C) and the rate is much higher for 2-pentyne than for 1-pentyne. The first products of the hydrogenation are 2-*cis*-pentene and 1-pentene, respectively. The product distributions during the course of a typical hydrogenation experiment of 2-pentyne at 80° C catalysed by $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}/Al_2O_3$ are shown in Figs. 2a and 2b, respectively. In Figs. 3a and 3b the product distributions during the hydrogenation of 2-pentyne catalysed by $Rh_2(CO)_4Cl_2$ and $Rh_2(CO)_4Cl_2/Al_2O_3$ are shown. It can be seen that in the presence of $Rh_4(CO)_{12}$ the rate of disappearance of

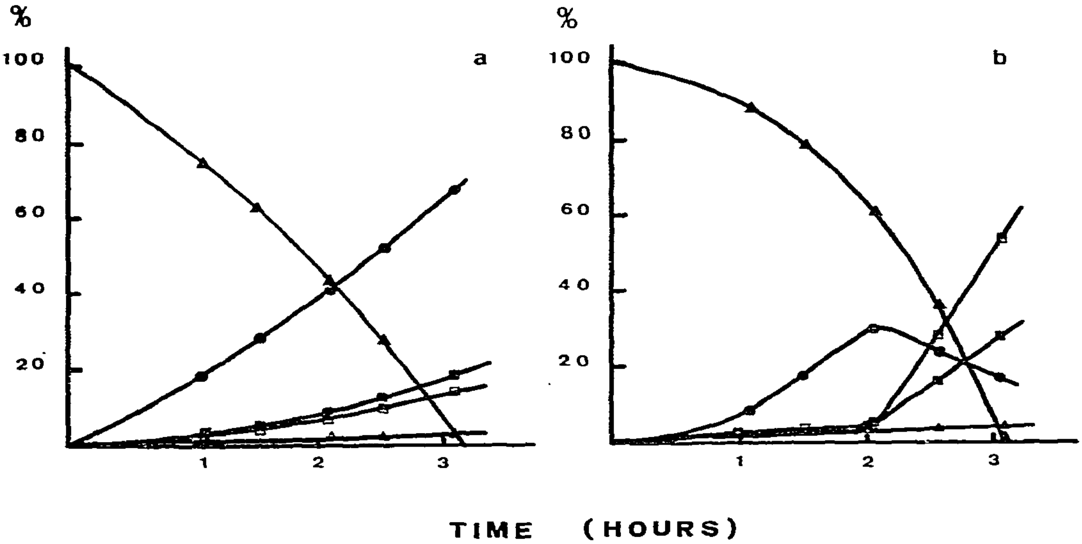

Fig. 2. Hydrogenation of 2-pentyne catalysed by $Rh_4(CO)_{12}$ (a) and $Rh_4(CO)_{12}/Al_2O_3$ (b) at 80° C. ▲ 2-pentyne; ● 2-*cis*-pentene; ■ 2-*trans*-pentene; △ 1-pentene; □ pentane.

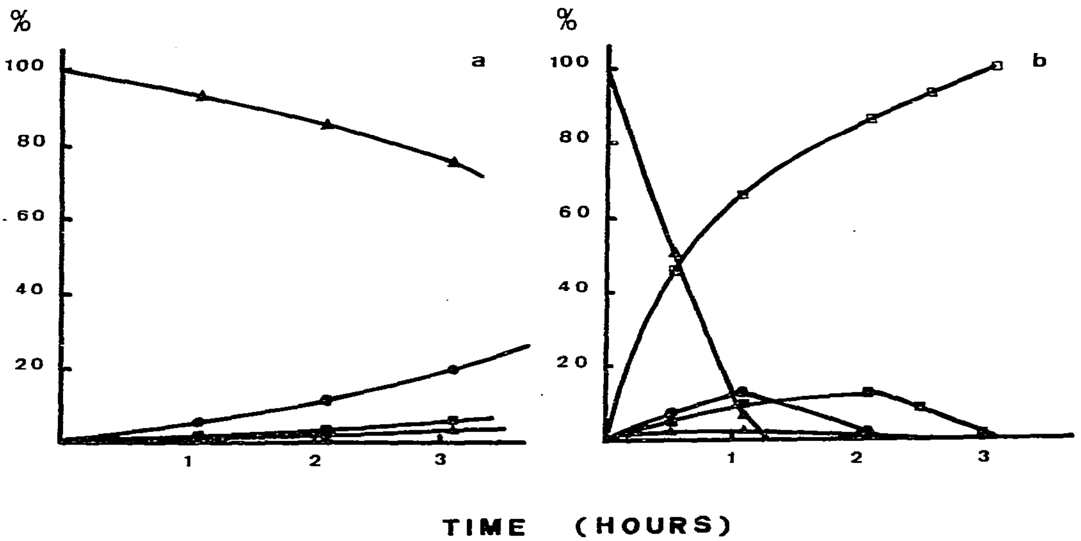

Fig. 3. Hydrogenation of 2-pentyne catalysed by $Rh_2(CO)_4Cl_2$ (a) and $Rh_2(CO)_4Cl_2/Al_2O_3$ (b) at 80°C. ▲ 2-pentyne; ● 2-*cis*-pentene; ■ 2-*trans*-pentene; △ 1-pentene; □ pentane.

2-pentyne does not change significantly upon going from the homogeneous to the heterogenised system. For $Rh_2(CO)_4Cl_2$, in contrast, an increased activity is observed for the heterogenised system.

The most significant difference between the homogeneous and heterogenised systems consists in the product distribution after a substantial percentage of the pentynes has undergone hydrogenation. In Table 1 is shown the percentage of the various species present after 3 h reaction at 80°C. The use of the homogneous catalysts leads to a build up of 2-*cis*-pentene or 1-pentene (from 2-pentyne and 1-pentyne, respectively) while in the presence of the bound catalysts the pentenes formed in the first stages of the reaction are rapidly converted into pentane.

In considering the causes of the differing behaviour of homogeneous and Al_2O_3-bound catalysts it is helpful to note the results obtained for the hydrogenation of 2-pentyne in the presence of $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}/Al_2O_3$ at 50°C. Fig. 4 shows that under these experimental conditions there is a progressive decrease of the reaction rate with time for the homogeneous system, but an increase with time for the heterogenised catalyst.

Some insight into the causes of the greater production of pentane can also be gained from the hydrogenation of pentenes catalysed by the rhodium clusters free in solution or bound to Al_2O_3. Toluene solutions of $Rh_4(CO)_{12}$ catalyse a rapid isomerisation at 40°C of 2-*cis*-pentene and of 1-pentene, followed by hydrogenation of the resulting mixture of pentenes to pentane, which accounts for 70% of the mixture within two hours. Much lower isomerisation and hydrogenation rates are observed for the reaction catalysed by the $Rh_4(CO)_{12}/Al_2O_3$ system. For 2-*trans*-pentene the rates of isomerisation and hydrogenation are much lower both in the homogeneous $Rh_4(CO)_{12}$ and in the $Rh_4(CO)_{12}/Al_2O_3$ systems (10% isomerisation to 2-*cis*-pentene after 2 h at 40°C for both sys-

TABLE 1

PRODUCT DISTRIBUTION (%) AFTER 3 h REACTION AT 80°C IN THE PRESENCE OF 1 atm H_2

Catalyst	Substrate	Pentyne	2-*cis*-Pentene	2-*trans*-Pentene	1-Pentene	Pentane
$Rh_4(CO)_{12}$	2-pentyne	5	64	17	2	12
$Rh_4(CO)_{12}/Al_2O_3$	2-pentyne	4	17	26	3	47
$Rh_4(CO)_{12}$	1-pentyne	95	<1	<1	4	<1
$Rh_4(CO)_{12}/Al_2O_3$	1-pentyne	88	<1	<1	8	3
$Rh_2(CO)_4Cl_2$	2-pentyne	76	17	3	2	2
$Rh_2(CO)_4Cl_2/Al_2O_3$	2-pentyne	—	—	—	—	100
$Rh_2(CO)_4Cl_2$	1-pentyne	98	<1	<1	1	<1
$Rh_2(CO)_4Cl_2/Al_2O_3$	1-pentyne	94	<1	<1	5	1

tems). Upon standing at room temperature (20° C) overnight some 40% of the pentenes is converted into pentane by $Rh_4(CO)_{12}/Al_2O_3$. Only trace amounts of pentane are formed with the homogeneous system.

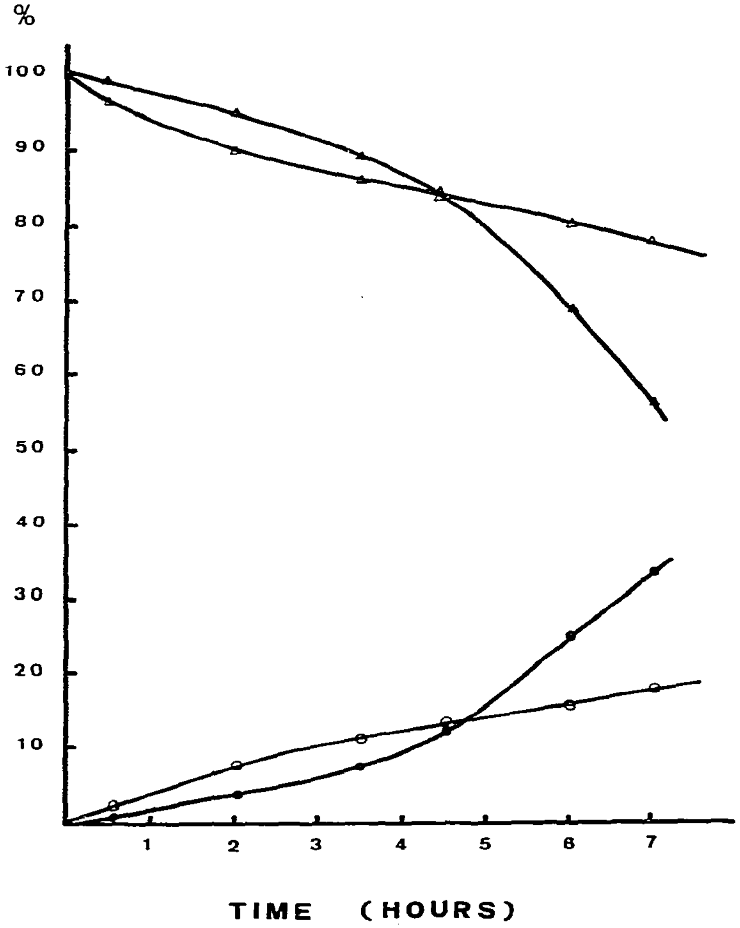

Fig. 4. Hydrogenation of 2-pentyne at 50°C catalysed by a toluene solution of $Rh_4(CO)_{12}$ (△ 2-pentyne; ○ 2-*cis*-pentene) and by $Rh_4(CO)_{12}/Al_2O_3$ (▲ 2-pentyne; ● 2-*cis*-pentene).

Similar experiments conducted on the $Rh_2(CO)_4Cl_2$ and $Rh_2(CO)_4Cl_2/Al_2O_3$ systems show that the isomerisation and hydrogenation of 2-*cis*-pentene occur with comparable rates in the presence of $Rh_2(CO)_4Cl_2$ and $Rh_2(CO)_4Cl_2/Al_2O_3$ systems. In contrast, conversion of 1-pentene and 2-*trans*-pentene into isomers and then into pentane is much faster in the presence of the heterogenised systems.

Discussion

The identity of the IR spectra of $Rh_4(CO)_{12}$, $Rh_2(CO)_4Cl_2$ and $Rh_6(CO)_{16}$ after adsorption on Al_2O_3 suggests that the symmetry of Rh centres is the same for the three catalysts once they are bound to the support. A similar spectrum was reported by Knozinger and Kumpf [8] for $Rh_6(CO)_{16}$ stabilised by attachment to chemically modified silica surfaces. Two IR bands were also reported by Bilhou et al. [10] for $Rh_6(CO)_{16}$ on silica, and attributed to $Rh^I(CO)_2$ centres connected by weak interactions.

The three rhodium clusters on Al_2O_3 were also studied by Smith et al. [17], although under different experimental conditions. These authors interpreted the identity of the spectra of $Rh_6(CO)_{16}$, $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ on Al_2O_3 as due to a conversion of the latter two complexes into $Rh_6(CO)_{16}$, catalysed by the basic oxide surface. In our experiments, however, we have found that the IR spectra are not changed from those reported in Fig. 1 when acidic Al_2O_3 is used in adsorption experiments. IR data on $Rh_2(CO)_4Cl_2/\eta\text{-}Al_2O_3$, obtained under conditions different from ours, have been reported recently [13].

Both rhodium clusters seem to be fairly thermally stable when heated under 1 atm H_2, since the characteristic IR adsorptions are retained. However, the difficulty of a quantitative evaluation of the adsorptions is such that we cannot completely rule out that a small amount of metal is produced by a limited decomposition of the metal carbonyls.

$Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$, either in solution or bound to Al_2O_3, are active catalysts for the hydrogenation of triple bonds and the rate is significantly dependent upon the position of the bond, internal isomers being hydrogenated more rapidly than the external isomers. This behaviour, while contrasting with that commonly observed for monometal complexes [18,19], agrees well with that we previously reported for $H_4Ru_4(CO)_{12}$ and its substituted derivatives with phosphorous-donor ligands [20,21].

Of particular interest is the enhanced activity of both rhodium catalysts when bound to Al_2O_3 towards the conversion to pentane of pentenes resulting from the initial hydrogenation of pentynes.

Several factors could account for this behaviour. For example: a) higher activity towards the hydrogenation of double bonds of the two rhodium clusters bound to Al_2O_3 compared with their homogeneous counterparts; b) deactivation of the catalysts under the conditions used when employed in solution as opposed to their stabilisation on Al_2O_3; c) enhancement of the activity of $Rh_4(CO)_{12}/Al_2O_3$ and $Rh_2(CO)_4Cl_2/Al_2O_3$, during the course of the reaction, mediated by some unknown process or modification of the catalysts; d) partial disruption of the clusters on Al_2O_3, causing the separation of metal particles during the reaction.

Given the complexity of the systems we cannot decide which of the possibilities outlined above is operative. From the results obtained in the hydrogenation of pentenes, we can conclude that hypothesis (a) does not apply to the $Rh_4(CO)_{12}/Al_2O_3$ system since the homogeneous counterpart is found to be more active towards the hydrogenation of pentenes when freshly introduced into the reaction vessel. A similar conclusion cannot be drawn for the $Rh_2(CO)_4Cl_2/Al_2O_3$ system, for which a higher conversion rate is observed for the hydrogenation of both pentynes and pentenes than for the corresponding homogeneous system. The hydrogenation experiments performed at 50°C in the presence of $Rh_4(CO)_{12}$ and $Rh_4(CO)_{12}/Al_2O_3$ favour hypotheses (b) and (c), although they do not provide any indication of the mechanism of the activation of the supported cluster as an hydrogenation catalyst. Moreover, the IR spectra indicate some thermal stability of the supported cluster, which contrasts with the instability of $Rh_4(CO)_{12}$ in solution [22], but as noted above, do not exclude the possibility that traces of metal are formed following a partial disruption of the clusters according to hypothesis (d). In view of the impossibility of performing a direct determination of traces of metal on Al_2O_3, we carried out a few experiments in order to evaluate the activity of pyrolysed clusters in the hydrogenation of 2-pentyne and 1-pentyne.

The metal particles deposited on Al_2O_3 following pyrolysis of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ anchored on the inorganic support are very active for the hydrogenation of both 2- and 1-pentyne, even at room temperature. They do not, however, display the selectivity towards the hydrogenation of 2-pentyne which is observed with non-pyrolysed Al_2O_3-anchored clusters. In contrast, the hydrogenation rate is slightly higher for 1-pentyne (which is virtually completely converted into pentane within 90 min) than for 2-pentyne (20% left after 90 min).

These results suggest that the active species present in $Rh_4(CO)_{12}/Al_2O_3$ and $Rh_2(CO)_4Cl_2/Al_2O_3$ systems are not metal particles deposited on Al_2O_3. This is further confirmed by the fact that neither $Rh_4(CO)_{12}/Al_2O_3$ nor $Rh_2(CO)_4Cl_2/Al_2O_3$ catalyses the hydrogenation of toluene to methylcyclohexane, which is a very sensitive test for the presence of metal particles [23]. Experiments under our experimental conditions on pyrolysed clusters showed that less then 1% conversion of the clusters into metal particles would be detected by this test.

In spite of the difficulties of explaining the modifications of the catalytic activity of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ when bound to Al_2O_3, one significant observation can be drawn from this study. This is that although the two rhodium clusters seem to give similar active centers on Al_2O_3, as indicated by the IR spectra, they display a completely different behaviour as catalysts for the hydrogenation of pentynes.

Experimental

$Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ were prepared as described in the literature [24,25] from $RhCl_3 \cdot n\ H_2O$ (Johnson and Matthey). 2-Pentyne (Merck), and 1-pentyne (Fluka) were redistilled and checked for purity by GLC.

The γ-alumina was from Strem and had a specific area of 150 m^2/g.

In some preliminary experiments, Al_2O_3 was treated under vacuum at 100°C for 1 h prior to use; the bulk of the experiments was, however, performed with the omission of this step. Adsorption of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ on γ-Al_2O_3 was performed at room temperature by bringing 2 cm^3 of a toluene solution of the metal carbonyls (0.40 mg/cm^3) into contact with 200 mg of Al_2O_3. The uptake on the support was monitored colorimetrically and was complete in less than one hour.

Some samples of $Rh_4(CO)_{12}$ and $Rh_2(CO)_4Cl_2$ bound on Al_2O_3 were heated under vacuum at about 500°C for 1 h in order to pyrolyse the clusters, and the activities toward the hydrogenation of 2-pentyne were then examined.

Hydrogenation experiments were run in glass vials with a GC septum, as previously described [20,26] at temperatures within the range 30—80°C. The molar ratio [Rh]/[pentyne] was 1/50. Samples were withdrawn during the reaction and the product distribution was determined by GLC as previously described [20].

IR spectra of catalysts bound on Al_2O_3 were recorded with Nujol mulls on a Beckman IR 4230 spectrophotometer.

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