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HYDROGENATION OF CONJUGATED DOUBLE BONDS OF *trans*-1,3-PENTADIENE CATALYSED BY $Rh_2Cl_2(CO)_4$ IN SOLUTION AND ANCHORED TO γ-Al_2O_3 *

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Summary

Hydrogenation under mild conditions (1 atm H_2 and 60—80°C) of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ in toluene solution and by $Rh_2Cl_2(CO)_4$ anchored on γ-Al_2O_3 has been investigated. Both the homogeneous and the heterogenised catalysts display a good specificity towards hydrogenation of the external double bond of the conjugated diene system. A slow inactivation of the supported catalyst occurs during the hydrogenation, but it cannot be attributed to reaction of the catalyst with the substrate since it occurs also when $Rh_2Cl_2(CO)_4$ is heated at 70°C under 1 atm H_2. Partial substitution of CO ligands of $Rh_2Cl_2(CO)_4$ by triphenylphosphine leads to a reduction of the activity of the homogeneous catalyst but does not alter its specificity. Triphenylphosphine can either increase or decrease the activity of the heterogenised catalyst depending on whether its introduction into the system precedes or follows the anchorage of $Rh_2Cl_2(CO)_4$ on Al_2O_3.

Introduction

Transition metal carbonyl compounds anchored on polymeric and inorganic supports are receiving increasing attention, not only because their study can lead to better understanding of surface interactions of heterogeneous metal catalysts with small molecules but also because of their practical value, arising from the possibility of improved activity and selectivity compared with the corresponding homogeneous systems [1—5]. Moreover, they combine advantages of homogeneous and heterogeneous catalysts since, on the one hand, they

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* Dedicated to the memory of Professor Paolo Chini.

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can be tailored to meet particular catalytic requirements and, on the other, no time consuming and expensive processes for the separation of the products from the catalyst are required.

As part of our studies on the catalytic activity of metal cluster compounds [6—9], we are evaluating the influence of inorganic supports on their activity and selectivity. In a previous paper [10] we compared the behaviour of $Rh_2Cl_2(CO)_4$ in solution and anchored on γ-Al_2O_3 when used to catalyse the hydrogenation of terminal and internal triple bonds in 1- and 2-pentyne, respectively. We describe below a comparative study of the hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ in toluene solution or anchored on γ-Al_2O_3 ($Rh_2Cl_2(CO)_4/Al_2O_3$). The reactivity and the selectivity of these two catalytic systems were the features of interest, rather than the nature of the species formed on the surface of the support in the steps which follow the adsorption of the metal carbonyl. Alumina was used in its fully hydroxylated form since drastic thermal treatments had to be avoided in order to reduce the gap between the conditions under which this study was performed and those relevant to its use in practical catalytic applications.

Results and discussion

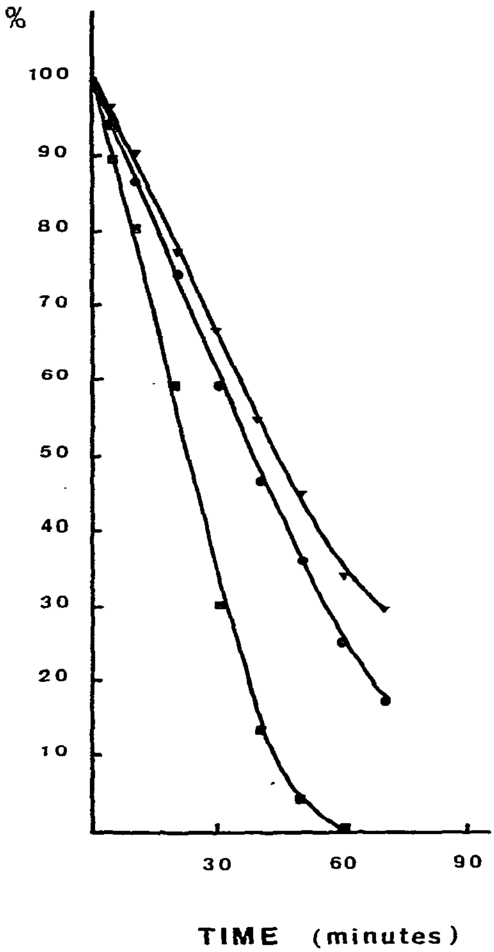
$Rh_2Cl_2(CO)_4$ rapidly hydrogenates *trans*-1,3-pentadiene under mild conditions (1 atm H_2 and temperatures between 60 and 80°C) both in solution and anchored on Al_2O_3. In Figs. 1 and 2 the percentage of remaining *trans*-1,3-pentadiene is shown as a function of reaction time for the $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(CO)_4/Al_2O_3$ systems, respectively, at temperatures of 60, 70 and 80°C. Initial hydrogenation rates, calculated from the tangent to the curves at time zero, are listed in Table 1. Although the activity of the supported catalyst is higher than that of the homogeneous system during the very first stages of the reaction, it undergoes a rapid decrease which is not paralleled by a similar one when the hydrogenation is carried out in solution. As a result, during the first 20 minutes of reaction the homogeneous system overtakes the heterogeneous one, to give a faster overall hydrogenation of the substrate.

The partial loss of activity of the supported catalyst towards hydrogenation of *trans*-1,3-pentadiene is not due to competition between substrate and products for active sites, since it can also be observed after removal of products in a recycling experiment in which the supported catalyst was recovered after 90

TABLE 1

INITIAL RATES OF HYDROGENATION OF *trans*-1,3-PENTADIENE CATALYSED BY $Rh_2Cl_2(CO)_4$ AND $Rh_2Cl_2(CO)_4/Al_2O_3$ UNDER 1 atm H_2. MOLAR RATIO [SUBSTRATE]/[CATALYST] = 42

Catalyst	Initial rates (mmol h^{-1})		
	Temperature (°C)		
	60	70	80
$Rh_2Cl_2(CO)_4$	30	42	60
$Rh_2Cl_2(CO)_4/Al_2O_3$	42	63	96



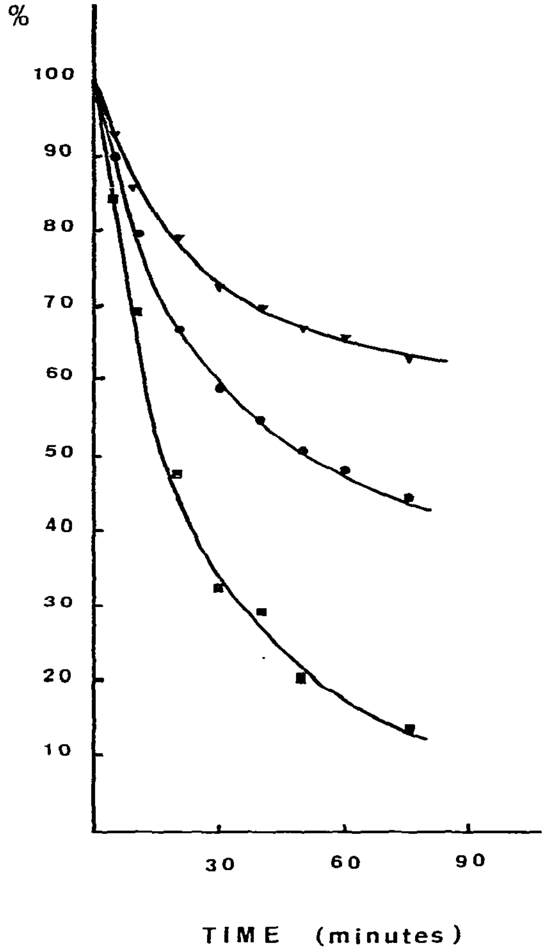


Fig. 1. Hydrogenation of *trans*-1,3-pentadiene catalysed by a toluene solution of $Rh_2Cl_2(CO)_4$ under 1 atm H_2 at 60°C (▼), 70°C (●) and 80°C (■). Ordinate: percentage of residual *trans*-1,3-pentadiene: abscissa: time in minutes.

Fig. 2. Hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ anchored on Al_2O_3, under 1 atm H_2 at 60°C (▼), 70°C (●) and 80°C (■). Ordinate: percentage of residual *trans*-1,3-pentadiene; abscissa: time in minutes.

minutes reaction (cycle 1) and freed from substrate and products. Fresh *trans*-1,3-pentadiene was then introduced into the reaction vial and its disappearance was measured (cycle 2). The results of this experiment are reported in Fig. 3 and show the slightly decreased activity of the recycled catalyst. A similar loss of activity is also observed when $Rh_2Cl_2(CO)_4$ is heated at 70°C for 90 min in the absence of the substrate and, therefore, it cannot be simply attributed to a modification of the catalyst as a result of its reaction with the substrate. Also IR spectra of Al_2O_3-supported $Rh_2Cl_2(CO)_4$ recorded after reaction at 70°C for two hours in the presence of *trans*-1,3-pentadiene indicate that no change has occurred in the supported catalyst, at least within the limits of sensitivity of the method. (In contrast, under homogeneous phase reaction conditions, par-

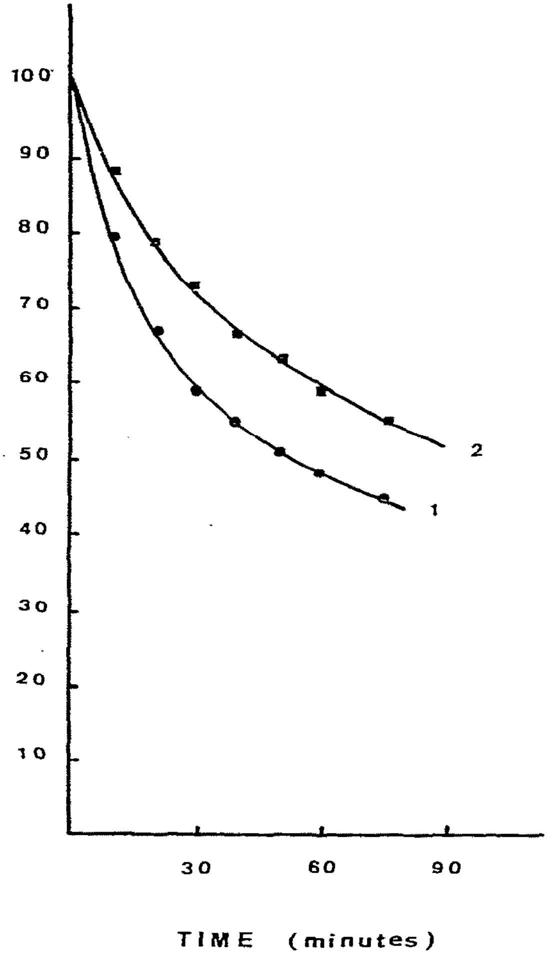


Fig. 3. Hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ supported on Al_2O_3 under 1 atm H_2 at 70°C. Ordinate: percentage of residual *trans*-1,3-pentadiene; abscissa: time in minutes. Curve 1: first cycle; curve 2: second cycle. For further explanation, see text.

tial replacement of CO ligands of $Rh_2Cl_2(CO)_4$ by the substrate can be detected by IR spectroscopy.) Hence thermal modification of the supported catalyst, leading to a less active species, must occur. As we have shown in a previous paper [10] however, no significant change in the IR spectrum is observed when $Rh_2Cl_2(CO)_4/Al_2O_3$ is heated at 80°C for 1 hour under 1 atm H_2. Decomposition of the carbonyl with separation of metal particles can be excluded, since none of the samples was active towards hydrogenation of toluene. This test is a very sensitive method for detecting trace amounts of metal [10,11].

Of particular interest is the analysis of products resulting from the hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ and by $Rh_2Cl_2(CO)_4/Al_2O_3$. In Table 2 are shown the product distributions determined after 1 hour at 60, 70 and 80°C in the presence of the homogeneous and of the anchored catalysts. The major product obtained by the hydrogenation of *trans*-1,3-pentadiene is *trans*-2-pentene arising from the hydrogenation of the exter-

TABLE 2

PRODUCT DISTRIBUTION AFTER 1 HOUR IN THE PRESENCE OF 1 atm H_2

Catalyst	Temperature (°C)	Products (%)		
		1-pentene	*trans*-2-pentene	*trans*-1,3-pentadiene
$Rh_2Cl_2(CO)_4$	60	11.45	54.47	34.08
$Rh_2Cl_2(CO)_4$	70	14.18	60.94	24.88
$Rh_2Cl_2(CO)_4$	80	17.11	82.89	tr.
$Rh_2Cl_2(CO)_4/Al_2O_3$	60	4.48	29.88	65.64
$Rh_2Cl_2(CO)_4/Al_2O_3$	70	9.38	41.93	48.68
$Rh_2Cl_2(CO)_4/Al_2O_3$	80	12.40	72.55	15.05

nal double bond, while hydrogenation of the internal double bond, leading to 1-pentene, occurs to a lesser extent. The ratio between *trans*-2-pentene and 1-pentene is about 5—6 for both catalysts, and is not significantly altered by changing the temperature. Only trace amounts of *cis*-2-pentene (approximately 1%) are present, and are indicative of the small extent of isomerisation. In none of the samples analysed was pentane present. From these observations it can be deduced that hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ in toluene solution and by $Rh_2Cl_2(CO)_4$ anchored on Al_2O_3 occurs, with good specificity, mainly at the external double bond of the conjugated diene system. The absence of pentane from the reaction mixture indicates that hydrogenation of the diene occurs only when pentadiene and pentenes are present together, irrespective of the position of the remaining double bond. It is noteworthy that when $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(CO)_4/Al_2O_3$ were used as catalysts for the hydrogenation of pentynes, the internal triple bond of 2-pentyne was hydrogenated at a higher rate than the external triple bond of 1-pentyne [10].

The influence of added CO on initial hydrogenation rates is shown in Table 3. In all cases, even small amounts of CO cause an inhibition, which is larger for the homogeneous system. A similar decrease of hydrogenation rate following the addition of CO had been observed for pentynes in the presence of $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(CO)_4/Al_2O_3$ as catalysts, and a reasonable explanation of such an effect is that the formation of active sites occurs via the release of a CO ligand from the metal carbonyl.

TABLE 3

INFLUENCE OF CO PRESSURES ON INITIAL RATES OF HYDROGENATION OF *trans*-1,3-PENTADIENE CATALYSED BY $Rh_2Cl_2(CO)_4$ AND BY $Rh_2Cl_2(CO)_4/Al_2O_3$ IN THE PRESENCE OF 1 atm H_2 AT 70°C

Catalyst	$P_{(CO)}$(Torr)	Initial rate (mmol h^{-1})
$Rh_2Cl_2(CO)_4$	0	42
$Rh_2Cl_2(CO)_4$	2.2	4.4
$Rh_2Cl_2(CO)_4$	4.3	1.0
$Rh_2Cl_2(CO)_4/Al_2O_3$	0	63
$Rh_2Cl_2(CO)_4/Al_2O_3$	2.2	13
$Rh_2Cl_2(CO)_4/Al_2O_3$	4.3	3.5

Addition of triphenylphosphine (PPh_3) has a different effect on hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ than on that catalysed by $Rh_2Cl_2(CO)_4/Al_2O_3$. For the homogeneous system (Fig. 4), when the addition of PPh_3 is immediately followed by introduction of *trans*-1,3-pentadiene, the disappearance of substrate follows curve 1 in Fig. 4. The overall effect of added PPh_3 is that of a substantial reduction of the hydrogenation rate, which can be attributed either to a lower activity of the PPh_3-substituted cluster or to a competition between substrate and phosphine for the same active sites on the catalyst, or both. The operation of both factors together is favoured by the downward curvature of the plot. In curve 2 of Fig. 4 the disappearance of *trans*-1,3-pentadiene is reported for a sample to which the substrate was added to a solution of $Rh_2Cl_2(CO)_4$ pre-heated with an equimolar amount of PPh_3 at

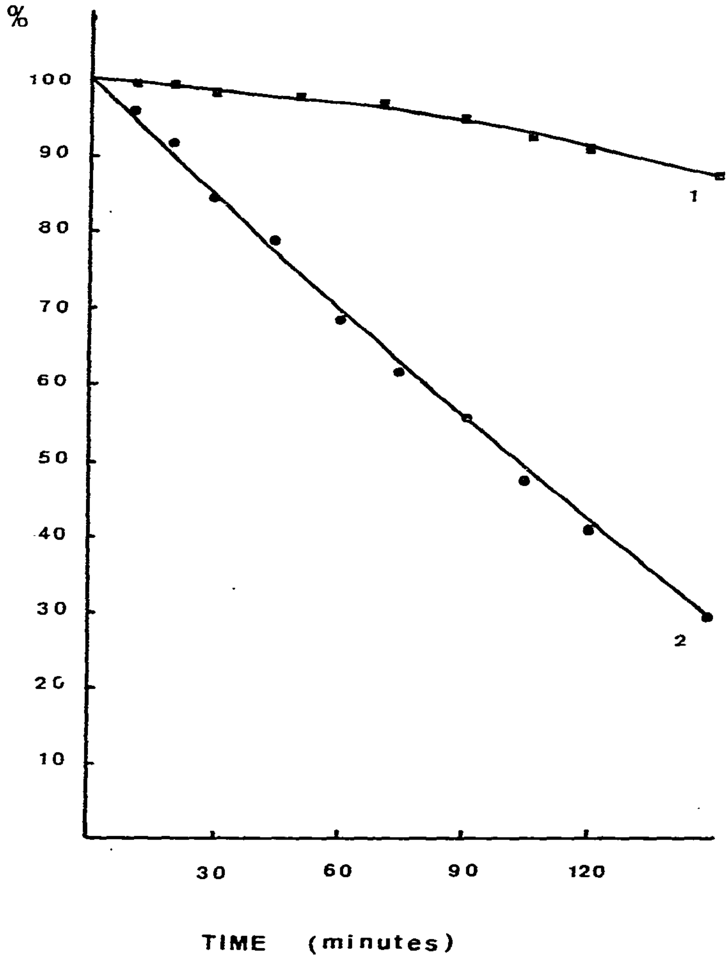


Fig. 4. Hydrogenation of *trans*-1,3-pentadiene catalysed by a toluene solution of $Rh_2Cl_2(CO)_4$ in the presence of PPh_3 under 1 atm H_2 at 70°C. Molar ratio $[Rh_2Cl_2(CO)_4]/[PPh_3] = 1$. Ordinate: percentage of residual pentadiene; abscissa: time in minutes. Curve 1: no thermal treatment of the solution containing $Rh_2Cl_2(CO)_4$ and PPh_3 before the addition of substrate. Curve 2: solution containing $Rh_2Cl_2(CO)_4$ and PPh_3 heated at 70°C for 2 hours before the addition of substrate.

70°C for 2 hours. Under these conditions competition between PPh_3 and the substrate is avoided, since the substitution takes place prior to the addition of substrate and the activity of substituted catalyst is measured. The IR spectra indicate, by comparison with published data [12,13], that the solution at this stage contains mostly the monosubstituted dinuclear species $Rh_2Cl_2(CO)_3PPh_3$, though the presence of some monosubstituted mononuclear species $RhCl(CO)_2$-PPh_3 cannot be excluded. The rate of disappearance of *trans*-1,3-pentadiene in the presence of the monosubstituted catalyst is substantially lower than that found for the unsubstituted one but higher than that indicated by curve 1. The low activity of the sample of curve 1 is thus due to the joint effect of competition and substitution. The lower catalytic activity of the substituted carbonyl compound can be related to the increased electron density on the metal.

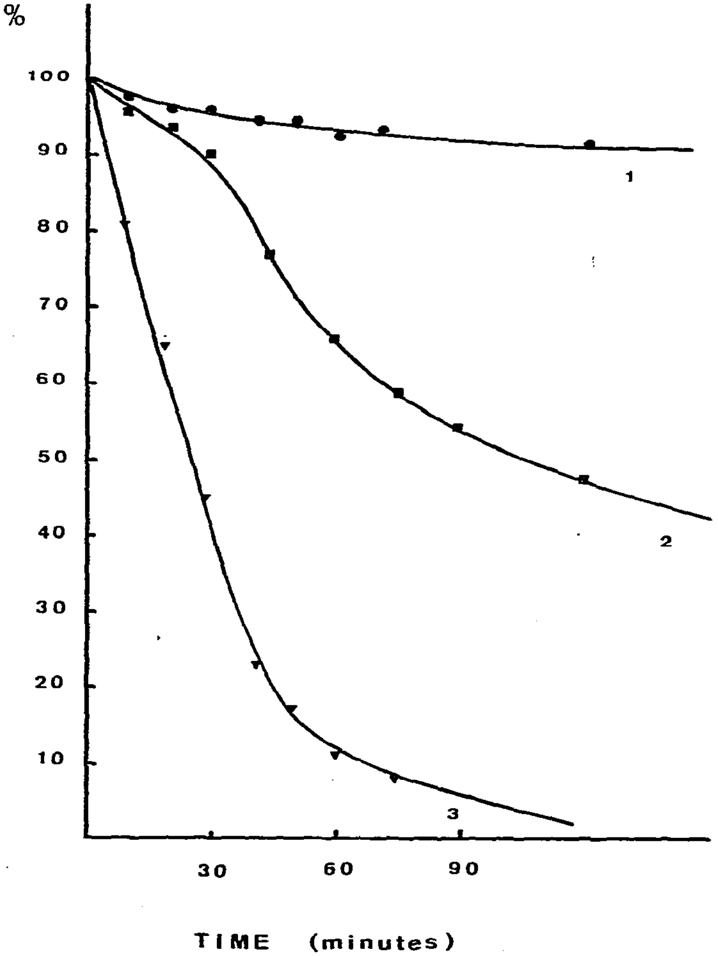


Fig. 5. Hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4$ anchored on Al_2O_3, in the presence of PPh_3 under 1 atm H_2 at 70°C. Molar ratio $[Rh_2Cl_2(CO)_4]/[PPh_3] = 1$. Ordinate: percentage of residual pentadiene; abscissa: time in minutes. Curve 1: addition of PPh_3 followed the anchorage of $Rh_2Cl_2(CO)_4$ on Al_2O_3; curve 2: PPh_3 and $Rh_2Cl_2(CO)_4$ mixed immediately before the anchorage; curve 3: Al_2O_3 kept in contact with PPh_3 for 10 hours before the anchorage of $Rh_2Cl_2(CO)_4$.

The behaviour of anchored $Rh_2Cl_2(CO)_4$ systems containing PPh_3 is more complex, since the catalytic activity depends on the detail of the sample preparation. Hydrogenation of *trans*-1,3-pentadiene catalysed by $Rh_2Cl_2(CO)_4/PPh_3/Al_2O_3$ systems is depicted in Fig. 5. Curve 1 refers to a sample for which addition of PPh_3 followed the anchorage of the carbonyl compound to the support, curve 2 to a sample in which PPh_3 was present during the anchorage, and curve 3 to one for which treatment of Al_2O_3 with PPh_3 preceded the anchorage. For samples 2 and 3 the uptake of $Rh_2Cl_2(CO)_4$ by Al_2O_3 was slow compared with that of samples which did not contain phosphine. These results indicate that PPh_3 can bring about two changes in the catalytic system; viz. (a) substitution at Rh centres, and (b) modification of the surface properties of the support. Curve 1 is, in fact, indicative of a low activity of PPh_3-substituted $Rh_2Cl_2(CO)_4$ anchored on Al_2O_3, and curve 3 is indicative of the high activity of the catalyst obtained by anchoring $Rh_2Cl_2(CO)_4$ on Al_2O_3 treated with PPh_3. Curve 2 of Fig. 5 probably represents a situation intermediate between those of curves 1 and 3. In none of the systems containing PPh_3 is the ratio between *trans*-2-pentene and 1-pentene significantly changed from that when the unmodified $Rh_2Cl_2(CO)_4$ and $Rh_2Cl_2(CO)_4/Al_2O_3$ systems are used.

On the basis of the results it can be concluded that anchorage of $Rh_2Cl_2(CO)_4$ to Al_2O_3 does not alter its specificity towards the preferential hydrogenation of the external double bond of *trans*-1,3-pentadiene. The easier separation of the catalyst from the reaction products is, however, partially counterbalanced by a slow inactivation of the anchored system. Of special interest is the increased catalytic activity of $Rh_2Cl_2(CO)_4$ bound to Al_2O_3 which has been pretreated with PPh_3.

Experimental

$Rh_2Cl_2(CO)_4$ was prepared as previously described [14] from $RhCl_3 \cdot n\ H_2O$ (Johnson Matthey).

trans-1,3-Pentadiene (Fluka) was checked for purity by GLC and did not require any further purification. Triphenylphosphine was from Fluka. Analytical grade toluene from Carlo Erba was dried over molecular sieves and redistilled.

The γ-Al_2O_3 (Merck) had a specific area of 130 m^2/g and was used in its fully hydroxylated form. The adsorption of the metal carbonyl onto the alumina and the hydrogenation experiments were performed as previously described [7,8,10]. The molar ratio $[Rh_2Cl_2(CO)_4]/[trans\text{-}1,3\text{-pentadiene}]$ was 1/42, and reaction temperatures were in the range 60—80°C. Samples were withdrawn during the reaction, and the percentage of residual *trans*-1,3-pentadiene, as well as the product distribution were determined by GLC at 55°C on a 4 m column of 20% silicone oil 702 on Chromosorb P, 60—80 mesh, and at 20°C on a 2 m column of 11% $AgNO_3$ and 21% phenylacetonitrile on Chromosorb P, 60—80 mesh. Blank tests were carried out, under identical experimental conditions, on γ-Al_2O_3 in the presence and in the absence of PPh_3. In none of the cases was the support found to catalyse hydrogenation of *trans*-1,3-pentadiene.

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