Platinum Metals Complex Catalysts for Liquid-Phase Hydrogenations

NOVEL CATALYSTS UTILISING ALIPHATIC AMINES AND RELATED SYSTEMS

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Results of the syntheses and applications of platinum metals complex catalysts, which are uniquely active for the liquid-phase hydrogenation of unsaturated organic compounds, such as olefins, dienes, acetylenes and aromatics, are described. The platinum metals complex catalysts are synthesised by the interaction between platinum metals compounds and aliphatic amines with sufficiently long alkyl groups (C_8 and higher). Similarities are shown in the production of palladium-, platinum-, and rhodium-based catalysts, which involves the formation of hydride ligands, using the hydrogen atoms of the alkyl groups, and the specific catalytic behaviour of each metal is described. Examples of synergistic effects for these platinum group metal catalysts and some of their related systems are discussed.

In spite of the considerable amount of work that has been undertaken on the hydrogenation of unsaturated organic compounds, it is still the subject of intensive investigations, with the platinum group metals continuing to be the most common components in hydrogenation catalysts, as well as in catalysts of other processes. As an example of this, at the first European Congress on Catalysis, "EUROPACAT I", held in September 1993, nine out of the fifteen symposia featured catalysis using the platinum metals to some extent, and thirteen of the fifteen papers at the symposium on metallic and bimetallic systems described the activities of platinum group metals (1). Metal complexes proved to be very successful in the construction of promising new systems that are capable of operating under much milder conditions than traditional heterogeneous catalysts.
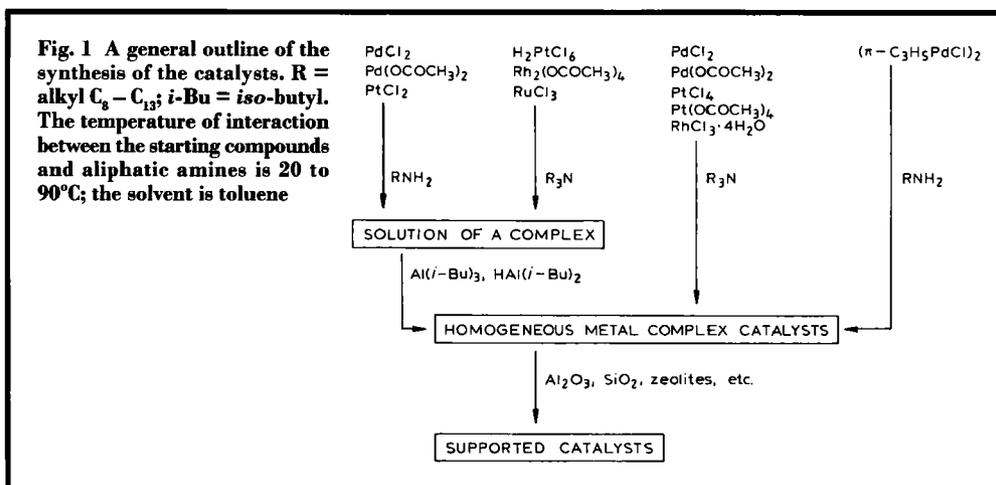
Strictly speaking, the only platinum metal complex systems which are of interest are those whose high specific activity, stability and length of operation, as well as high selectivity, compensate for the additional cost needed to recover the noble metal and synthesise the initial com-

pound, since the usual methods of catalyst regeneration cannot be applied to such systems.

In recent years a new approach to catalytic hydrogenation, based on using complexes of platinum metal compounds with aliphatic amines containing eight or more carbon atoms in alkyl radicals, has been developed at our Institute. As numerous metal complex catalysts good for hydrogenation contain phosphines or phosphites, bonded to the metal with a considerable contribution of the back donation using the d-orbitals of phosphorus, the initial purpose of this work was to determine to what extent replacing traditional phosphorus containing ligands by nitrogen containing ligands, for which this type of bonding is impossible, would affect the catalytic properties. From a practical standpoint, the selected amines looked more suitable, since they are less toxic than the usual phosphorus containing ligands.

Interactions between Components of the Catalyst System

The general outline of the synthesis is given in Figure 1. The interaction in toluene between the initial platinum metals compounds, which

Fig. 1 A general outline of the synthesis of the catalysts. R = alkyl $C_8 - C_{13}$; *i*-Bu = *iso*-butyl. The temperature of interaction between the starting compounds and aliphatic amines is 20 to 90°C; the solvent is toluene

are insoluble in aromatic media, and the aliphatic amines under an argon atmosphere for tens of hours resulted in a gradual transfer of metal species into solution, due to the high affinity of long alkyl groups for the solvent. In certain cases (on the left side of the scheme which is shown above as Figure 1) the solution which was produced did not show catalytic properties, but hydrogenation activity appeared after treating the complexes which are formed with a rather strong reducing agent (usually an organoaluminium compound). Because of the high affinity of the reduction products for the solvent, these catalytically active species also remain soluble. In this way efficient palladium- (2–5), platinum- (6, 7), rhodium- (8), and ruthenium-based (8, 9) catalysts have been obtained.

In the most interesting cases (on the right in Figure 1), it is the interactions of the initial platinum metals compounds with aliphatic amines that lead to the formation of highly active homogeneous catalysts (the systems: palladium salts (10–12), rhodium trichloride (8, 9, 12, 13) or platinum compounds (12, 14–16) with tertiary amines, and π-allyl palladium chloride with primary amines (17)).
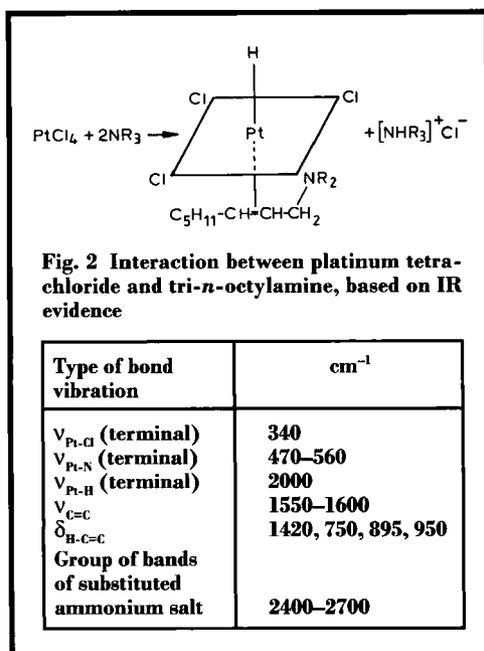
An important property of all these systems is that they can be readily heterogenised, by the direct contact of a solution of the homogeneous catalyst with the outgassed surface of a mineral support, without activity decrease (in most cases

with an increase of the turnover frequency) (14, 18–20). Here, we have used conventional values of turnover frequency, calculated as the number of moles of the substrate that reacted per one g-atom of the metal per hour.

Infrared and NMR spectral studies of the interaction of the initial palladium, platinum and rhodium compounds with aliphatic amines in an aromatic solvent showed the formation of hydride ligands on the metal during the first stage of the reaction. It is of interest that the source of the hydrides on the metal is both from the hydrogen atoms in the amino groups of the primary or secondary amines and from the hydrogen of the alkyl groups of tertiary amines.

For the reaction between palladium chloride and a tertiary amine, the spectral data indicate the formation of a bridged hydride ($v_{Pd-H-Pd}$ = 1590 to 1600/cm) and co-ordination bonding between palladium and nitrogen (v_{Pd-N} = 490/cm) (9). At the same time double bonds arise in one of the alkyl groups as a result of a hydrogen transfer to the metal ($v_{C=C}$ = 1610/cm, ^{1}H NMR signal for -CH=CH- at 5.3×10^{-6}, δ-scale (9)).

The simultaneous formation of hydride ligands on the metal and a double bond in an alkyl group of the amine has also been observed in the platinum tetrachloride-tri-*n*-octylamine system (Figure 2). It can be seen from this Figure that the participation of a second amine

Fig. 2 Interaction between platinum tetrachloride and tri-*n*-octylamine, based on IR evidence

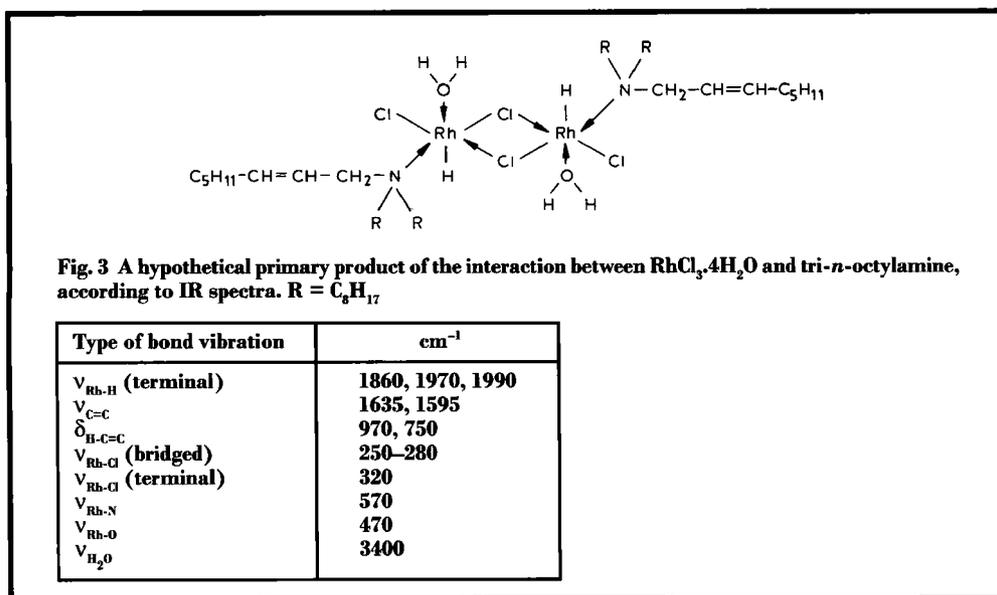| Type of bond vibration	cm^{-1}
ν_{Pt-Cl} (terminal)	340
ν_{Pt-N} (terminal)	470–560
ν_{Pt-H} (terminal)	2000
$\nu_{C=C}$	1550–1600
$\delta_{H-C=C}$	1420, 750, 895, 950
Group of bands of substituted ammonium salt	2400–2700

molecule helps to link a proton being abstracted from the first amine molecule (simultaneously with the hydride) to form a salt of the substituted ammonium.
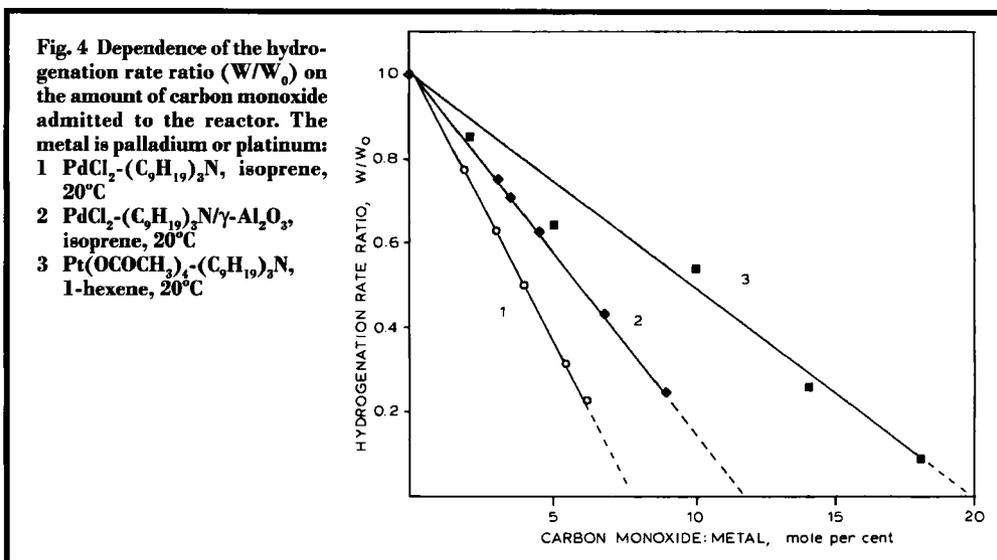
A primary product of the interaction of rhodium trichloride, having four molecules of

water of crystallisation, with tri-octylamine has hydride ligands on rhodium and a C=C double bond in one of the alkyl groups of the tertiary amine, according to IR spectroscopic data, see Figure 3. According to NMR data, the double bond is located at the second carbon atom of the alkyl group (13).

Similar data were obtained for ruthenium systems. Thus, based on these results it can be concluded that the formation of hydride ligands on the metal during the interaction between the initial compound and the aliphatic amine, using the hydrogen of an alkyl group of the amine, is a general feature typical for all the platinum metals studied. However, we do not think that the hydride, formed at an early stage of the interaction between the components, can react with a multiple bond of the substrate to start a catalytic cycle. Instead, it initiates a chain of reactions that finally results in the formation of metal complex species (also perhaps of hydride character) which are capable of activating molecular hydrogen.

Further interactions between the components of the catalyst system are accompanied by more profound changes, the details of which are so far still not clear. However, there is some indirect evidence in favour of the formation

Fig. 3 A hypothetical primary product of the interaction between RhCl$_3$.4H$_2$O and tri-*n*-octylamine, according to IR spectra. R = C$_8$H$_{17}$

Type of bond vibration	cm^{-1}
ν_{Rh-H} (terminal)	1860, 1970, 1990
$\nu_{C=C}$	1635, 1595
$\delta_{H-C=C}$	970, 750
ν_{Rh-Cl} (bridged)	250–280
ν_{Rh-Cl} (terminal)	320
ν_{Rh-N}	570
ν_{Rh-O}	470
ν_{H_2O}	3400

Fig. 4 Dependence of the hydrogenation rate ratio (W/W_0) on the amount of carbon monoxide admitted to the reactor. The metal is palladium or platinum:
1 $PdCl_2$-$(C_9H_{19})_3N$, isoprene, 20°C
2 $PdCl_2$-$(C_9H_{19})_3N/\gamma$-Al_2O_3, isoprene, 20°C
3 $Pt(OCOCH_3)_4$-$(C_9H_{19})_3N$, 1-hexene, 20°C

of polynuclear or cluster structures.

During the final stages of the interaction of platinum tetraacetate with tri-n-nonylamine, we could not detect the presence of co-ordinated amine molecules or acetate groups. However, absorption bands were observed which are characteristic of both terminal and bridged hydride groups, and may suggest that plane polynuclear structures are formed.

Data on the inhibition of the hydrogenation reaction by carbon monoxide, see Figure 4, show that complete blocking of the active sites takes place at relatively low ratios of carbon monoxide:palladium and carbon monoxide:platinum (less than 20 per cent). These values were obtained by extrapolating the linear plots to the zero hydrogenation rate. The results agree with the concept that the formation of active sites occurs within the polynuclear or cluster structures.

However, we have never observed any broadening in the NMR signals due to the formation of metallic particles suspended in the aromatic solvent (even for rhodium species), although there are indications in the literature that the interaction between $RhCl_3$ and $N(C_8H_{17})_4B(C_2H_5)_3H$ in tetrahydrofuran leads to the formation of colloidal particles of metallic rhodium protected by tetraalkylammonium groups, which are very active in liquid-phase hydrogenation (21, 22).

A feature very characteristic of the platinum group metal catalysts prepared by our method is their exceptionally high catalytic activity, which sometimes attains tens of thousands of catalytic acts per one metal atom per hour.

Palladium-Based Catalysts

The most active catalysts are palladium-based and their field of application is for the selective hydrogenation of conjugated dienes and acetylenes into olefins. Analysis of kinetic data on the hydrogenations (23) – zero order in substrates and selectivities attaining 100 per cent at conversions close to 100 per cent – allows a conclusion to be made about complete coverage of the active sites by the co-ordinated substrates under equilibrium conditions of co-ordination (chemisorption). A quantitative criterion of the reaction selectivity is the factor $R = k_1K_1/k_2K_2$, where k_1 and k_2 are the rate constants for the hydrogenation of a substrate and an olefin product (both in the co-ordination state); and K_1 and K_2 are the corresponding equilibrium constants of co-ordination on the active sites (or adsorption coefficients in the case of supported catalysts). It follows from the analysis that a selectivity of 98 per cent can be attained at a conversion of 98 per cent if R is as high as 150

Table I

Activities of Catalysts at 20°C, Based on the System PdCl$_2$-(C$_9$H$_{19}$)$_3$N/Carrier (0.05% Pd by weight)

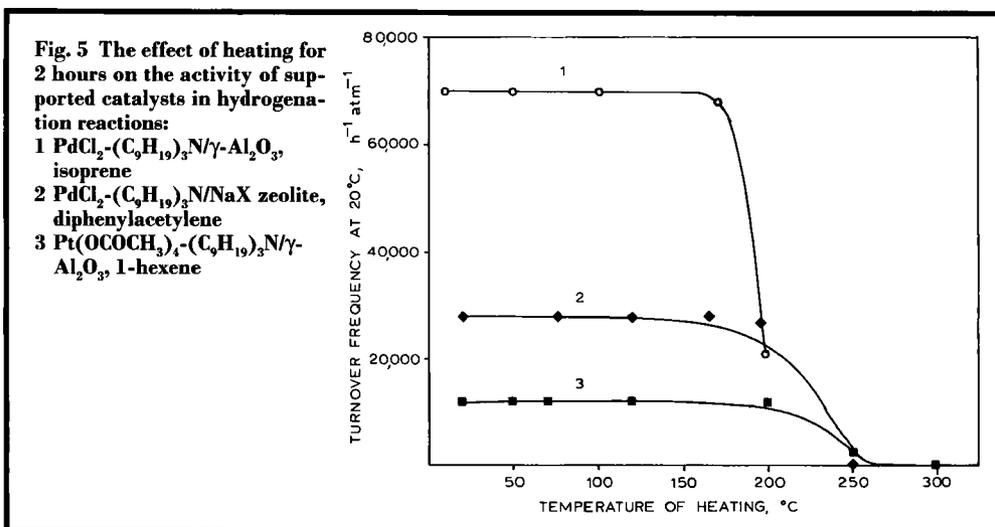| Substrate	Solvent	Carrier	Turnover frequency, h^{-1} × atm^{-1}
Isoprene	Hexane	γ-Al$_2$O$_3$	121,000
Isoprene	Hexane	SiO$_2$	137,000
Isoprene	DMFA	γ-Al$_2$O$_3$	49,000
Isoprene	-	γ-Al$_2$O$_3$	94,000
Cyclopentadiene	Toluene	γ-Al$_2$O$_3$	38,000
Cyclopentadiene	Hexane	γ-Al$_2$O$_3$	57,000
Cyclopentadiene	-	γ-Al$_2$O$_3$	45,000
3-Heptyne	Toluene	γ-Al$_2$O$_3$	32,000
3-Heptyne	Hexane	γ-Al$_2$O$_3$	49,500
R-CH(OH)-C≡CH	Toluene	NaX zeolite	13,100
R-CH(OH)-C≡CH	Heptane	NaX zeolite	8,800

All kinetic runs with platinum metal systems were carried out at constant hydrogen pressure in a swinging reactor under conditions where an increase in the swinging frequency did not affect the rate of hydrogen consumption
DMFA = dimethylformamide; R = 2-tetrahydrofuryl

(23). Dilution of a diene with olefins reduces the selectivity but, nevertheless, selectivity was still found to be high (94 per cent) even when butadiene was hydrogenated as a 4 per cent impurity in a mixture of butenes up to conversions close to 100 per cent (24).

Homogeneous catalysts are sensitive to hydroxyl-containing substances and can be used only for the hydrogenation of unsaturated hydrocarbons. Supporting palladium-based systems upon fine powders of mineral carriers considerably increases their stability and makes it possible to hydrogenate functional derivatives of conjugated dienes and acetylenes; for example, acetylenic alcohols into olefinic ones (25). In contrast to traditional Lindlar's catalysts (metallic palladium on calcium carbonate partially poisoned by quinoline or lead salts), our catalysts proved to be more active by almost two orders of magnitude.

Table II

Effect of Poisons on the Catalyst System PdCl$_2$-(C$_9$H$_{19}$)$_3$N as a Homogeneous System or Supported on γ-Alumina during the Hydrogenation of 3-Heptyne into 3-Heptene at 20°C

Inhibitor	Inhibitor/Pd, mole/mole	Turnover frequency, h^{-1} × atm^{-1}	
		Homogeneous	Supported
None	0	25,800	32,500
Water	20	1,200	32,000
Triphenylphosphine	40	23,900	32,500
Thiophene	50	20,400	30,800
Dihexylsulphide	1	18,000	30,100
Dihexylsulphide	50	0	3,500
Hexylmercaptan	1	0	3,200

Fig. 5 The effect of heating for 2 hours on the activity of supported catalysts in hydrogenation reactions:
1 PdCl$_2$-(C$_9$H$_{19}$)$_3$N/γ-Al$_2$O$_3$, isoprene
2 PdCl$_2$-(C$_9$H$_{19}$)$_3$N/NaX zeolite, diphenylacetylene
3 Pt(OCOCH$_3$)$_4$-(C$_9$H$_{19}$)$_3$N/γ-Al$_2$O$_3$, 1-hexene

Hydrogenation of disubstituted acetylenes is stereoselective: diphenylacetylene and 4-octyne yield cis-stilbene (95 per cent) and cis-4-octene (99 per cent), respectively.

Activities of supported catalysts in various solvents are given in Table I. It can be seen that the best results have been obtained either in saturated hydrocarbons or without using solvent.

Table II summarises data on poisoning homogeneous and supported catalysts (26). It can be seen that water and triphenylphosphine do not affect the activity of supported catalysts; thiophene slightly suppresses their activity at a molar ratio poison:metal = 50. Other poisons have a much more pronounced effect, and the supported systems are more resistant to poisoning than the homogeneous ones.

The supported catalysts retain their activity after heating at up to 150 to 200°C, as is shown in Figure 5 (curves 1 and 2). Due to the chemisorptive nature of the support, an upper limit in the percentage of metal on the carrier is observed. Usually this value does not exceed 0.2 per cent by weight.

For practical purposes palladium-containing catalysts are of interest for use in such liquid-phase processes as the hydropurification of olefins to remove traces of dienes and acetylenes, for the hydrogenation of acetylenic fragments into olefinic fragments in a number of inter-mediates during the production of vitamins, and in the hydrogenation of vegetable oils.

For sunflower seed oil, it is necessary to hydrogenate one double bond of the linoleic acid fragments in the corresponding glycerides. Double bonds in linoleic acid are not conjugated. Nevertheless, it was shown that rapid isomerisation occurred at first on our palladium catalysts, resulting in the formation of a system of conjugated double bonds, and this was followed by selective hydrogenation to produce a fragment of oleic acid and some of its isomers. Compared to modern industrial nickel catalysts it is possible to use 0.1 per cent of the amount of metal and to decrease the reaction temperature by almost 100°C (27).

Platinum- and Rhodium-Containing Catalysts

Platinum-containing catalysts are to some extent even more interesting than the palladium-based ones. The reason is that unlike the large number of palladium systems described in the literature, only a relatively small number of platinum systems have been reported, and most of them have serious disadvantages. They are unstable towards molecular oxygen and moisture, they have low activity, they can hardly be heterogenised and they catalyse migration of C=C double bonds during hydrogenation.

Table III

Hydrogenation of 1-Hexene at 20°C in the Presence of Platinum-Based Catalysts: Homogeneous or Supported on γ-Alumina (0.06 % Pt by weight)

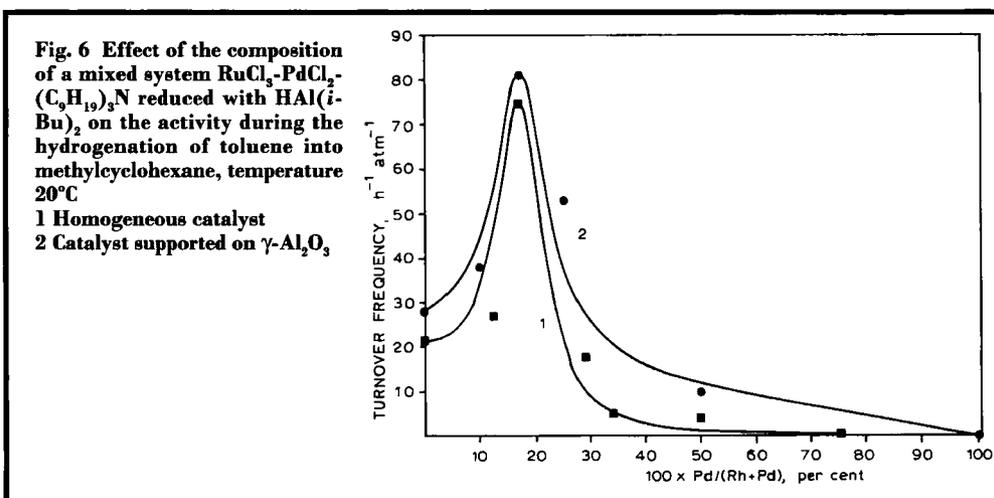| System	Turnover Frequency, $h^{-1} \times atm^{-1}$	
	Homogeneous	Supported
H_2PtCl_6-$(C_9H_{19})_3N$-$HAl(i\text{-}Bu)_2$	17,000	20,500
$PtCl_4$-$(C_8H_{17})_3N$-H_2	12,000	12,000
$PtCl_2$-$(C_8H_{17})_2NH$-$HAl(i\text{-}Bu)_2$	2,900	6,500
$PtCl_2$-$C_8H_{17}NH_2$-$HAl(i\text{-}Bu)_2$	21,400	32,600
$Pt(OCOCH_3)_4$-$(C_9H_{19})_3N$-H_2	10,600	11,600
$Pt(OCOCH_3)_4$-$(C_8H_{17})_2NH$	3,000	4,600

In our studies, however, the use of the interaction of platinum compounds, particularly the acetates of bi- and tetravalent platinum, with aliphatic amines allowed catalysts to be prepared which were stable to dioxygen and water, and which were capable of carrying out the complete hydrogenation of unsaturated substrates, such as olefins, dienes and acetylenes. For example, the platinum tetraacetate-trinonylamine system did not show any decrease in hydrogenation activity for 1-hexene when the molar ratio water:platinum was increased to 200. This last catalyst could be synthesised and stored in air.

As was the case with the palladium-based catalysts, supporting the platinum-containing species on the surface of mineral carriers (γ-alumina, silica, zeolites) increases their stability. In Figure 5 (curve 3), the activity of the supported platinum-based catalyst drops only after heating up to 200°C.

Table III shows the effect that a γ-alumina support has on catalyst activity. Most supported systems are more active, in terms of turnover frequency, than homogeneous systems. For some catalysts a preliminary treatment with molecular hydrogen was necessary to attain high activity, otherwise kinetic curves had induction periods with a subsequent slow increase in the hydrogenation rate.

An important property of the platinum-based catalysts is their relatively high activity, not only in hydrogenating α-olefins but also in hydrogenating olefins with internal double bonds. We now have some evidence that this property can be used for the hydrogenation of unsaturated polymers and attains quite good rates. It is noteworthy that the hydrogenation of α-olefins is zero order with respect to the substrate, whereas the first order law is typical for olefins with internal double bonds (14). The latter case may reflect a much lower coverage of the active sites.

Table IV

Hydrogenation of Olefins in the Presence of Rhodium-Based Catalysts

Catalyst system	Substrate	Turnover frequency, $h^{-1} \times atm^{-1}$
$RhCl_3.4H_2O$-$(C_8H_{17})_3N$	1-Hexene	26,000
$RhCl_3.4H_2O$-$(C_8H_{17})_3N/\gamma\text{-}Al_2O_3$	1-Hexene	52,400
$RhCl_3.4H_2O$-$(C_8H_{17})_3N/SiO_2$	1-Hexene	50,200
$RhCl_3.4H_2O$-$(C_8H_{17})_3N/Nd_2O_3$	1-Hexene	60,300
$RhCl_3.4H_2O$-$(C_8H_{17})_3N/\gamma\text{-}Al_2O_3$	Cyclohexane	20,100
$RhCl_3.4H_2O$-$(C_8H_{17})_3N/\gamma\text{-}Al_2O_3$	Cyclopentene	37,000

Fig. 6 Effect of the composition of a mixed system RuCl₃-PdCl₂-(C₉H₁₉)₃N reduced with HAl(*i*-Bu)₂ on the activity during the hydrogenation of toluene into methylcyclohexane, temperature 20°C
1 Homogeneous catalyst
2 Catalyst supported on γ-Al₂O₃

Very active rhodium-based catalysts (Table IV) could also be synthesised by this method. The activities of the systems studied during the hydrogenation of 1-hexene and cyclohexene are several times higher than those of "classical" catalysts – based on tris(tertiary phosphine)-chlororhodium (28–30). The catalysts are not of interest for the actual hydrogenation of linear olefins, since that reaction is accompanied by migration of the double bond in the substrate, but for their surprising ability of being considerably activated upon treatment with dioxygen and water (13).

Ruthenium-Containing Catalysts

The synthesis of ruthenium-based systems has made it possible to obtain highly active catalysts for the hydrogenation of aromatic rings. After reduction with di-*iso*-butylaluminium hydride, the ruthenium systems revealed unique catalytic properties for the hydrogenation of toluene into methylcyclohexane (31). It was established that additions of small amounts of palladium exerted a pronounced promoting effect, see Figure 6, whereas the palladium complex itself was totally inactive.

The superadditivity of catalytic properties (a "synergistic effect") for the mixed system was characterised by a rather sharp maximum which corresponded to an additive of 17 mole per cent palladium. Surprisingly, this was the case for both homogeneous and supported catalysts.
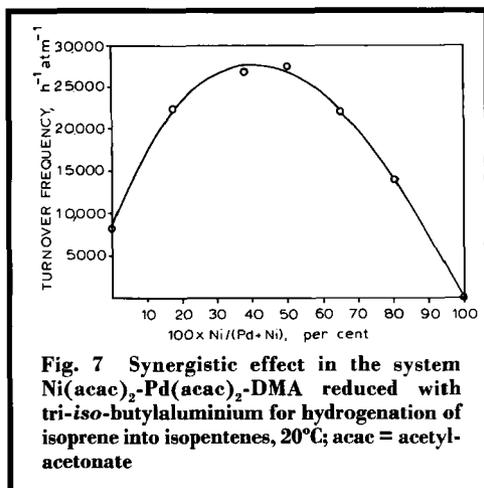
A comparison between the activity of our catalyst with data from the literature for a ruthenium hydride complex with a triphenylphosphine ligand, [RuHCl(η-C₆Me₆)(PPh₃)], which is active for the hydrogenation of benzene into cyclohexane (32), showed that its turnover frequency, according to our estimate, was 50/hour at 50°C and 50 atm. However, in our case, a turnover frequency of 80/hour was attained at 20°C and 1 atm, which demonstrates the advantages of our approach. A ten-fold increase in the hydrogen pressure up to 10 atm resulted in a proportional enhancement of the activity.

Synergistic Effects Caused by the Presence of a Non-Noble Metal

As the promotion effects of non-noble metals to catalysts are of most interest we have undertaken a search for a suitable bimetallic system which might be able to demonstrate the necessary type of synergistic effect. Unfortunately, palladium-nickel systems with tertiary amines proved to be useless because they did not display the superadditivity effect; the specific activity of this system was directly proportional to the mole fraction of the palladium complex.

The solution to this problem was found by using homogeneous binary palladium-nickel complex systems, prepared by the interaction

Fig. 7 Synergistic effect in the system Ni(acac)$_2$-Pd(acac)$_2$-DMA reduced with tri-*iso*-butylaluminium for hydrogenation of isoprene into isopentenes, 20°C; acac = acetylacetonate

of a mixture of the acetylacetonates of these metals with allene or 1,1-dimethylallene (DMA) and the subsequent treatment of the product, which has oligoallene ligands, with tri-*iso*-butylaluminium (33). The presence of the oligoallene ligands caused the "floatation effect", similar to that of higher amines, which provides the solubility in hydrocarbon media. These systems were also very active in the selective hydrogenation of conjugated dienes into olefins.
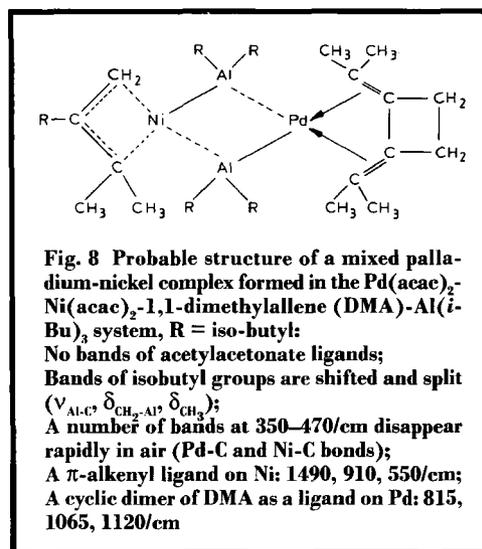
The dependence of the catalytic activity of the binary system on its composition during the hydrogenation of isoprene into isopentenes is shown in Figure 7. The plot shows the activity, based on the sum of both metals. It is clearly of superadditive character, the maximum activity being approximately three times as large as the activity of the pure palladium complex. The pure nickel complex was inactive.

Infrared spectroscopic data were used to explain some details of the interaction mechanism of the components in mono and bimetallic systems. The spectrum of the Pd(acac)$_2$-DMA-Al(*i*-Bu)$_3$ system did not contain any absorption bands characteristic of Al(*i*-Bu)$_3$, but all bands that are typical of aluminium acetylacetonate were present in the spectrum. The absence from the spectrum of relatively intensive bands at 1130, 980 and 910/cm indicated that there was a great change in the DMA in the complex (there were no bands characteristic

of monomeric and linear oligomeric forms of DMA). Similarly, no bands characteristic of a π-alkenyl complex of palladium were visible in the spectrum. As a hypothesis it could be suggested that a complex of palladium with a dimer of DMA, containing a four-member ring, was formed. Upon oxidation of the sample in air for 15 to 30 seconds, the intensity of the bands at 820, 1068, and 1136/cm sharply decreased; these were not bands for aluminium acetylacetonate. We suggest that these bands referred to a hypothetical palladium π-complex with a cyclic dimer of DMA. The bands above are not unlike those observed experimentally for a similar lithium complex.

The IR spectrum of the four-component system Ni(acac)$_2$-Pd(acac)$_2$-DMA-Al(*i*-Bu)$_3$ did not contain any bands characteristic of acetylacetonate ligands and free acetylacetone. Almost all the bands that are characteristic of Al(*i*-Bu)$_3$ were present, but they were greatly changed. A number of bands at 350 and 470/cm rapidly disappeared in air, indicating the presence of both palladium-carbon and nickel-carbon bonds.

The above-mentioned bands of the palladium complex at 820, 1068 and 1136/cm, hypothetically referring to a palladium π-complex with a dimer of DMA, were present in the spectrum of the mixed complex at 815, 1065 and

Fig. 8 Probable structure of a mixed palladium-nickel complex formed in the Pd(acac)$_2$-Ni(acac)$_2$-1,1-dimethylallene (DMA)-Al(*i*-Bu)$_3$ system, R = iso-butyl:
No bands of acetylacetonate ligands;
Bands of isobutyl groups are shifted and split (v_{Al-C}, δ_{CH_2-Al}, δ_{CH_3});
A number of bands at 350–470/cm disappear rapidly in air (Pd-C and Ni-C bonds);
A π-alkenyl ligand on Ni: 1490, 910, 550/cm;
A cyclic dimer of DMA as a ligand on Pd: 815, 1065, 1120/cm

1120/cm. However, there were also bands at 1490, 910 and 550/cm which could be assigned to a π-alkenyl bonding with nickel in the hypothetical structure shown in Figure 8.

Consequently, the presence of a second transition metal crucially changed the picture of the interaction between the components, and might result in the formation of active sites that are much more active than monometallic ones, due to their mixed structure. The fact that an example of such a bimetallic system was found (although not with amine containing systems) is very encouraging for a future search to find highly active catalysts involving a complex of a non-noble metal as a second component. This approach, which is often used for heterogeneous catalysis, is usually overlooked for use with metal complex systems, because very efficient ways of affecting catalytic properties already exist, such as the appropriate choice of ligand. It is interesting that results similar to ours were obtained with palladium-nickel alloy films for the catalytic hydrogenation of ethylene (34), although the observed effects differ mechanistically.

Conclusions

The data that have been presented show that interactions between compounds of the platinum group metals and aliphatic amines with sufficiently long alkyl groups lead to a new type of hydrogenation catalysts, which have a number of common features in their production and

a well-determined specificity inherent in each metal. It appears that the "drawbacks" of aliphatic amines, caused by their inability to participate in building up multiple bonds with the metal of a complex (unlike phosphines and phosphites) are well compensated for by the high reactivity of the hydride complexes that are formed during the interaction between the components of the catalyst system. As a result of the interaction to form hydride complexes, rather complicated catalytically active polynuclear structures may arise, under conditions which favour the solubility of these species.

Although most of our results were only obtained on a laboratory scale, the very high activities, selectivities, and relative inertness to poisons of these platinum group catalyst systems make them promising for commercial use.

Extending the scope of the catalysts, by using bimetallic systems to find synergistic effects, and of substrates involving organic compounds with functional groups to be hydrogenated, is one of the main aims for the future.

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Activity of Platinum-Containing Electrodes Enhanced

The extraction of zinc from its ores by electrolysis in aqueous solution provides a high purity product and is the method used for winning a substantial proportion of world zinc output. The process is energy intensive, but energy efficiency was not a consideration in the design of existing electrowinning plants, which are generally sited close to sources of cheap hydroelectricity. Now, however, various attempts are being made to develop more efficient processes.

In conventional electrowinning of zinc oxygen gas is evolved in the cell, as an unnecessary by-product, and this accounts for a substantial part of the cell voltage. In a new process this oxygen evolution is replaced by the anodic oxidation of sulphur dioxide produced during the smelting process, or by the anodic oxidation of hydrogen. For this new process to be feasible the anode has to have high electrocatalytic activity for the oxidation of sulphurous acid. Previous work has demonstrated that after suitable activation amorphous nickel-valve metal

alloys containing 1 per cent platinum group metal, and other elements, display enhanced activity for anodic sulphite oxidation in a neutral borate buffer solution. Now the same investigators at the Institute for Materials Research at Tohoku University, Sendai, Japan, have reported on their evaluation of the effect of cathodic reduction on the catalytic activity for anodic oxidation of sulphite on electrodes prepared from amorphous nickel-valve metal-platinum group metal alloys (T. Mori, A. Kawashima, E. Akiyama, H. Habazaki, K. Asami and K. Hashimoto, *J. Appl. Electrochem.*, 1995, 25, (10), 953–961).

After immersion in hydrofluoric acid and subsequent cyclic voltammetry in sulphuric acid, their electrodes were subjected to galvanostatic cathodic reduction before assessment. Addition of platinum, together with rhodium, iridium or ruthenium, to amorphous nickel-40 niobium was found to be particularly effective in improving the catalytic activity for sulphite oxidation.