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On the mechanism of the platinum(0)–acid catalysed hydrogenation of alkenes

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Abstract

The hydrogenation of styrene promoted by the system [Pt(C_2H_4)(DPPB)]/acid is strongly affected by the nature of the solvent, the nature of the acid co-catalyst and the Pt/acid molar ratio. The highest catalytic activity is obtained in toluene working with methanesulfonic acid at a Pt/acid ratio = 1. The influence of the temperature and the hydrogen pressure on the catalytic activity has also been studied. The results indicate that at least two different catalytic systems operate. One of these accounts for the catalysis in the temperature range 25–35°C, while the other one is effective above 35°C. The catalytic activity of some model compounds has been also studied. ^{31}P-NMR spectroscopy demonstrates that the complexes [Pt{CH(CH_3)(C_6H_5)}(CH_3SO_3)(DPPB)] and [Pt(CH_3SO_3)$_2$(DPPB)] are present in the low-temperature catalytic cycle.

Key words: Platinum; Alkene; Catalysis; Hydrogenation

1. Introduction

We have previously reported [1,2] that platinum(0) complexes of the type [Pt(ethylene)(chelating diphosphine)] (chelating diphosphine: 1,4-bis-(diphenylphosphino)butane (DPPB) or (+)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)-DIOP)] in the presence of methanesulfonic acid catalyse the hydroformylation and the hydrogenation of unsaturated substrates.

As far as the hydrogenation reaction is concerned, the most interesting features are the activity in the hydrogenation of carbonyl groups in particular of aldehydes; and the oxidation state of the metal catalyst which is based on a platinum(0) species. In the literature there are only a few examples of platinum(0) complexes active in the hydrogenation of olefins [3–5] and mechanistic information about possible reaction intermediates involved in these catalytic processes is still scanty. In the present paper, we report a detailed investigation on the influence of some reaction parameters such as the metal-to-acid molar ratio, the nature of the solvent and of the acid co-catalyst, and the temperature and the pressure. Furthermore, the involvement of some specific reaction intermediates has been confirmed by comparing the catalytic activity of specifically synthesised model complexes with that of our system.

2. Results and discussion

2.1. *The catalytic activity of platinum(0)-acid system*

Since earlier studies [1,2] showed that our catalytic system also promotes the isomerization of alkenes, we have chosen styrene as the model substrate in the present study. Preliminary work demonstrated that the polymerisation of the substrate does not occur under the reaction conditions used.

The results of the hydrogenation experiments with different platinum-to-methanesulfonic acid molar ratios are collected in Table 1.

No ethylbenzene is formed in the absence of methanesulfonic acid. However, the addition of the acid to the system causes an enhancement of the catalytic activity until a maximum is reached when an acid to platinum molar ratio of 1/1 is used. Higher ratios cause a smooth decrease in the ethylbenzene yield.

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TABLE 1. Influence of the platinum/acid molar ratio on the hydrogenation rate

CH_3SO_3H (mmol)	Acid/Pt molar ratio	Ethylbenzene yield (%)
0	0	0
0.0125	0.25	24.9
0.025	0.5	30.1
0.0375	0.75	35.5
0.05	1	38.4
0.075	1.5	32.5
0.10	2	30.5
0.15	3	24.2

Styrene: 16 mmol; $[Pt(C_2H_4)(DPPB)]$: 0.05 mmol; acid: methanesulfonic acid; substrate/Pt molar ratio: 320; toluene: 20 ml; $P(H_2)$: 20 atm; T: 25°C; reaction time: 22 h.

The influence of the solvent on the catalytic activity is shown in Table 2.

The highest reaction rate is observed in toluene, a poor coordinating solvent of low polarity. In polar and more coordinating solvents, such as methanol, ethyl acetate, and dichloromethane, the system displays lower activities. In tetrahydrofuran the reaction is almost inhibited and in acetonitrile there is complete loss of activity due to extensive decomposition of the catalyst with formation of black material, probably metallic Pt.

The nature of the acid promoter plays an important role as indicated by the results obtained in the presence of some different acid co-catalysts (Table 3).

The best promoters are the closely related acids CH_3SO_3H and CF_3SO_3H which give systems displaying comparable activities. Other strong proton acids, such as sulphuric acid and trifluoroacetic acid, give rise to much less active systems, while the weak, coordinating acetic acid is not an effective co-catalyst.

The results of hydrogenation experiments carried out at different temperatures and under different hydrogen pressures are reported in Table 4.

Taken all together, these data indicate an intricate dependence of the catalytic activity on the various parameters. Thus, at 25°C an increase of the hydrogen pressure causes an enhancement of the reaction rate. However, the dependence of the reaction yield on the pressure is not linear since an asymptotic conversion of styrene (~ 70%) is obtained at the highest pressures. A similar trend is also displayed by the reactions carried out at 35°C, but now it is observed that an increase of the pressure to over 20 atm causes a less marked effect on the reaction rate. At 50°C, the catalytic activity becomes independent of hydrogen pressure, and the rate is lower than that observed at 35°C. At 80°C the system also displays independence of the hydrogen pressure. However, the temperature increase from 50 to 80°C is accompanied by a significant increase of reaction rate.

TABLE 2. Influence of the solvent on the catalytic hydrogenation of styrene

Solvent	Ethylbenzene yield (%)
Toluene	70.1
Dichloromethane	36.8
Ethyl acetate	47.0
Methanol	54.0
Acetonitrile	–
Tetrahydrofuran (THF)	7.6

Styrene: 16 mmol; $[Pt(C_2H_4)(DPPB)]$: 0.05 mmol; CH_3SO_3H: 0.05 mmol; substrate/Pt molar ratio: 320; solvent: 20 ml; $P(H_2)$: 80 atm; T: 25°C; reaction time: 22 h.

TABLE 3. Influence of the nature of the co-catalyst

Co-catalyst	Ethylbenzene yield (%)
CH_3SO_3H	70.1
CF_3SO_3H	68.7
H_2SO_4	15.2
CF_3COOH	4.5
CH_3COOH	0

Styrene: 16 mmol; $[Pt(C_2H_4)(DPPB)]$: 0.05 mmol; Pt/acid molar ratio: 1; substrate/Pt molar ratio: 320; solvent: 20 ml; $P(H_2)$: 80 atm; T: 25°C; reaction time: 22 h.

The data of Table 4 may be rationalised assuming the presence of at least two catalytically active systems, one, whose catalytic activity depends on the hydrogen pressure, and which operates in the temperature range 25–35°C, and a second, operating at temperatures above 35°C, displaying a catalytic activity independent of the hydrogen pressure.

2.2. *The catalytic activity of model complexes*

It is well known that electrophilic attack of Brönsted acid on an olefin coordinated to Pt^0 causes the formation of Pt^{II}-alkyl species [6–9]. Thus the reaction between $[Pt(C_2H_4)(DPPB)]$ (**1a**) and a stoichiometric amount of methanesulfonic acid gives the complex $[Pt(C_2H_5)(CH_3SO_3)(DPPB)]$ (**2a**), which has been characterised by elemental analysis (see Experimental

TABLE 4. Influence of temperature and pressure on the catalytic activity of system $[Pt(C_2H_4)(DPPB)]/CH_3SO_3H$

Pressure (atm)	Ethylbenzene yield (%)			
	25°C	35°C	50°C	80°C
20	41.0	48.5	45.3	89.2
50	63.4	59.0	45.6	92.4
80	70.3	60.4	46.3	90.1
100	68.6	57.3	48.6	92.3

Styrene: 16 mmol; $[Pt(C_2H_4)(DPPB)]$: 0.05 mmol; CH_3SO_3H: 0.05 mmol; substrate/Pt molar ratio: 320; toluene: 20 ml; reaction time: 22 h.

section) and NMR spectroscopy. The ^{31}P-NMR spectrum consists of an AX spin system flanked by ^{195}Pt satellites ($\delta(P_A) = 30.65$ ppm ($J(P_A\text{-}Pt) = 1689$ Hz), $\delta(P_X) = 10.58$ ppm ($J(P_X\text{-}Pt) = 5069$ Hz), $J(P_A\text{-}P_X) =$ 11 Hz. The coupling constants allow us to attribute the lower field resonance to the phosphorus atoms *trans* to the ethyl group [10].

The ^{1}H-NMR spectrum of **2a** is dynamic at room temperature, displaying (besides the resonances due to the other ligands) a complex multiplet centred at 1.47 ppm (2H by integration) which is attributed to the methylene group, and two broad resonances at 1.31 ppm (1H by integration) and 0.61 ppm (2H by integration). Irradiation of the signal at 0.61 ppm leads to a considerable decrease of the intensity of the signal at 1.31 ppm, indicating that these resonances arise from protons which are exchanging slowly. These observations lead us to attribute the signals at 1.31 and 0.61 ppm to the methyl protons. The broad profile of the signals and the results of a spin-saturation transfer experiment indicate that there is hindered rotation around the carbon–carbon bond of the ethyl group. The reason for such hindered rotation and for the downfield shift of the resonance of one of the methyl protons is unclear. An agostic interaction cannot be invoked because that would imply that signals at higher fields than TMS should be observed.

Spencer recently reported [11,12] that Pt-ethylene-diphosphine complexes (diphosphine = ^{t}Bu$_2$P(CH$_2$)$_n$P^{t}Bu$_2$ ($n = 2$ or 3), Cy$_2$P(CH$_2$)$_n$PCy$_2$ ($n = 2$ or 3), or 1,2-(^{t}Bu$_2$PCH$_2$)$_2$C$_6$H$_4$) can be protonated by non-coordinating acids to give Pt^{II}-ethyl cations. These species have been characterised as ethene-hydride or agostic ethyl complexes on the basis of variable-temperature multinuclear NMR studies and X-ray crystallography. A deeper insight into the coordination of the ethyl group in complex **2a** will probably be obtained from a study of its dynamic behaviour which is currently in progress. In addition to the above spectroscopic evidence, the formulation of complex **2a** is supported by its reaction with LiCl in dichloromethane which gives the known complex [PtCl(C$_2$H$_5$)(DPPB)] [10].

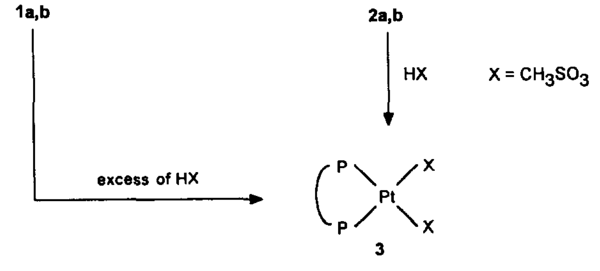
In complexes of the type **1a** the ethene ligand may be displaced by other alkenes [13]. Thus, treatment of complex [Pt(C$_2$H$_4$)(DPPB)] (**1a**) with a large excess of styrene affords the corresponding styrene platinum(0) complex [Pt(C$_8$H$_8$)(DPPB)] (**1b**) in moderate yield. This has been characterised by elemental analysis (see Experimental section) and NMR spectroscopy.

In the ^{1}H-NMR spectrum the alkene protons of styrene give rise to three distinct signals: complex multiplets centred at 3.35 ppm [$J(\text{H-Pt}) = 66$ Hz], 2.34 ppm [$J(\text{H-Pt})$ obscured by the resonances of the other ligands] and 2.13 ppm [$J(\text{H-Pt}) = 66$ Hz]. In keeping with the proposed formulation, the ^{31}P-NMR spectrum consists of an AB spin system flanked by platinum satellites ($\delta(P_A) = 23.11$ ppm, $\delta(P_B) = 22.98$ ppm, $J(P_A\text{-}P_B) = 62$ Hz, $J(P_A\text{-}Pt) = 3554$ Hz and $J(P_B\text{-}Pt) = 3531$ Hz). Both the ^{1}H- and ^{31}P-NMR data are consistent with those of other platinum complexes of this type reported in the literature [9,14].

Recent studies by Spencer and co-workers [14,15] have shown that the protonation of styrene platinum diphosphine complexes affords compounds containing η^3-benzyl ligands, which have been also structurally characterised. Accordingly, complex **1b** reacts with a stoichiometric amount of CH$_3$SO$_3$H to give the benzyl complex [Pt(CH(CH$_3$)Ph)(CH$_3$SO$_3$)(DPPB)] (**2b**) as inferred from analytical data and its ^{1}H-NMR spectrum. The latter displays a complex multiplet (3H by integration) centred at 0.96 ppm, which is attributed to the methyl group, and a complex multiplet at 3.00 ppm (1H) for the benzyl hydrogen in addition to the resonances due to the other ligands. More information on the coordination mode of the benzyl moiety can be obtained from the ^{31}P-NMR spectrum of **2b** which displays an AX spin system flanked by the ^{195}Pt satellites: $\delta(P_A) = 16.22$ ppm, $J(P_A\text{-}Pt) = 3145$ Hz, $\delta(P_X) = 20.24$ ppm, $J(P_x\text{-}Pt) = 5228$ Hz, $J(P_A\text{-}P_x) = 6.1$ Hz. In particular, the value of the P$_A$–Pt coupling constant agrees with the data reported by Spencer and is indicative of η^3-coordination since a much lower platinum–phosphorus coupling constant (~ 1600–1800 Hz) [16] is usually found in the case of a P atom *trans* to an alkyl group.

When complexes **1a** or **1b** are treated with an excess of methanesulfonic acid the complex [Pt(CH$_3$SO$_3$)$_2$(DPPB)] (**3**) is formed (Scheme 1).

Complex **3**, which can also be obtained by reaction of **2a** or **2b** with methanesulfonic acid, is best formulated as the bis-(aqua) complex [Pt(H$_2$O)$_2$(DPPB)(CH$_3$SO$_3$)$_2$] as indicated by its elemental analysis (see Experimental section) and NMR spectra. The ^{31}P-



Scheme 1.

TABLE 5. Influence of Pt/acid ratio on the ethylbenzene yield with various platinum catalyst

Catalyst precursor	Ethylbenzene yield (%)			
	Pt/Acid = 1/0	Pt/Acid = 1/1	Pt/Acid = 1/2	Pt/Acid = 1/3
$[Pt(C_2H_4)(DPPB)]$	0.0	38.4	30.5	24.3
$[Pt(C_2H_5)(CH_3SO_3)(DPPB)]$	40.3	24.7	25.6	–
$[Pt(CH_3SO_3)_2(DPPB)]$	27.5	26.8	–	–

Styrene: 16 mmol; platinum complex: 0.05 mmol; acid: methanesulfonic acid; substrate/Pt molar ratio: 320, toluene: 20 ml; $P(H_2)$: 20 atm; T: 25°C; reaction time: 22 h.

NMR spectrum of **3** registered in $CDCl_3$ at 298 K shows a singlet at 2.73 ppm flanked by ^{195}Pt satellites ($^1J(P\text{–}Pt) = 3904$ Hz). The large line width of this resonance (~ 80 Hz) suggests that this species is dynamic at room temperature. The ^1H NMR spectrum reveals a broad absorption in the range 4.7–3.2 ppm (4 protons by integration) in addition to the signals due to the phosphine and methanesulfonate protons. At 213 K, the last resonance moves to low fields and sharpens, giving rise to a singlet at 8.43 ppm (4 protons by integration), which we assign to water molecules coordinated to the metal. These findings suggest that at room temperature the water molecules coordinated to the metal are rapidly exchanging with molecules as solvent or methanesulfate anion. At 213 K also the ^{31}P NMR spectrum is not dynamic ($\delta P = 4.59$ ppm, $^1J(P\text{–}Pt) = 3875$ Hz). The presence of the water molecules is probably due to the fact that no particular care has been paid in order to avoid moisture during the work-up. Pt^{II} complexes of the type $[Pt(diphosphine)(H_2O)_2](CF_3SO_3)_2$ have been described previously [17,18] and in one case the X-ray structure has been reported [18], but no ^1H NMR data for the water protons have been so far reported.

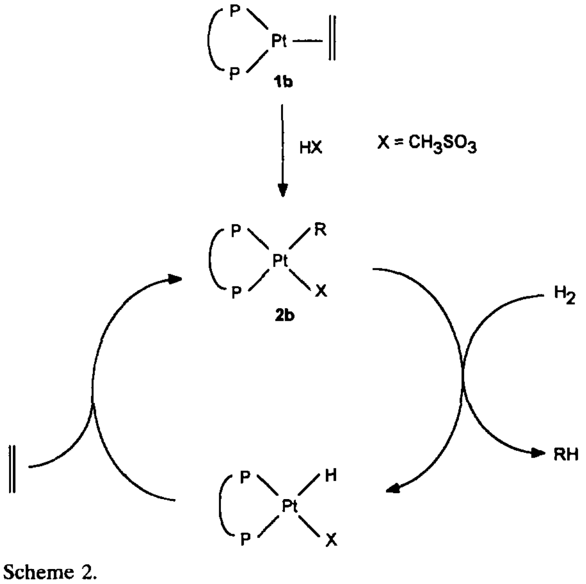
In order to verify the involvement of the alkyl-Pt^{II} complexes of type **2** in the catalytic cycle, we have used complex **2a** as catalyst in the presence of variable amounts of methanesulfonic acid. The relevant data are presented in Table 5 which reports for comparison purposes also the catalytic data obtained with complexes **1a** and **3**.

The catalytic activity of complex **2a** in the absence of any acid added, matches that of the system formed by **1a** and 1 equivalent of CH_3SO_3H. This equivalence of catalytic activity is also shown at higher acid-to-platinum ratios. For example, the ethylbenzene yield obtained with **2a** in the presence of 1 equivalent of methanesulfonic acid is very close to that found with **1a** and two equivalents of acid. The same catalytic activity is obtained by using complex **3** with no acid added. Furthermore, the systems formed by complex **1a** and 3 equivalents of acid, complex **2a** and 2 equivalents of acid and complex **3** and 1 equivalent of acid exhibit the same catalytic activity. These results suggest strongly that the catalytic processes involve the formation of the alkyl complex **2b** and its reaction with molecular hydrogen to give ethylbenzene and a hydrido-complex, as depicted in Scheme 2. The catalytic cycle is completed by the insertion of the substrate into the Pt–H bond to regenerate the alkyl complex.

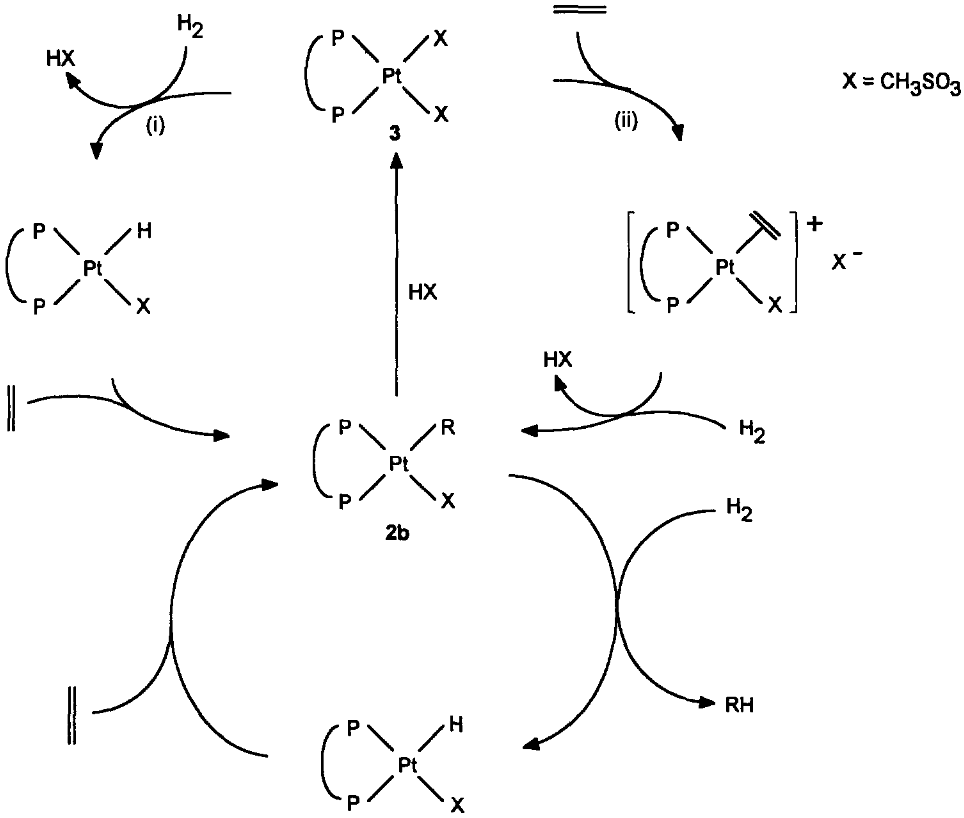
Although hydridoplatinum(II)-diphosphine complexes are rare [19,20], a series of hydrido-complexes of the type suggested in Scheme 2 has been recently synthesised by Spencer [12], who also reported the X-ray structure of the platinum hydrido-complex $[PtH(CF_3SO_3)\{^tBu_2P(CH_2)_3P^tBu_2\}]$ and its reaction with ethylene to afford the corresponding platinum ethyl complex.

The catalytic activity displayed by complex **3** is remarkable because the complex contains neither hydrido nor alkyl ligands. A possible catalytic cycle based on complex **3** is depicted in Scheme 3.

The process may proceed initially by one of the two routes (i) and (ii): (i) the heterolytic hydrogen activation is followed by olefin insertion to form an alkylplatinum(II) species and (ii) olefin coordination to the metal is followed by heterolytic hydrogen activation to



Scheme 2.



Scheme 3.

give the same type of intermediate. The catalytic cycle could be completed by the hydrogenolysis of the alkylplatinum(II) complex as in the case of Scheme 2, or by its reaction with the molecule of methanesulfonic acid formed in earlier steps. The heterolytic activation of hydrogen by platinum(II) complexes has been well documented by Pregosin and Ruegger [21], who demonstrated that $[PtCl(SnCl_3)(PPh_3)_2]$ reacts with H_2 to give the hydrido complex $[PtH(SnCl_3)(PPh_3)_2]$ and HCl.

A direct proof for the participation of complexes **2b** and **3** in the catalytic cycle has been obtained by the ^{31}P-NMR spectra of the solutions recovered after some catalytic runs carried out at 25°C under 20 atm of hydrogen in the presence of the system **1a** and 1 equivalent of CH_3SO_3H. These display two major resonances: the most important (relative abundance ~ 2) is the AX spin system of complex **2b**, the next (relative abundance ~ 1) is that of complex **3**. A few other resonances of low intensity which we have been unable to assign are also present. The presence of complex **3** is remarkable since its formation is not due to an inaccurate stoichiometric balance. The same type of ^{31}P NMR spectrum is obtained on using **2a** as catalyst. These findings indicate that during the catalytic process some "disproportionation" reactions take place, producing complex **3** and other species not containing methanesulfonate as required by the stoichiometry. However, efforts to detect and identify such species have been so far unsuccessful.

Above 25°C and with $P(H_2) > 20$ atm the system becomes even more complicated. Under reaction conditions different from those of Table 5 the catalytic activity of complex **2a** does not match that of the system complex **1a**/CH_3SO_3H. Table 6 presents the

TABLE 6. Influence of temperature and pressure on the catalytic activity of complex $[Pt(C_2H_5)(CH_3SO_3)(DPPB)]$

Pressure (atm)	Ethylbenzene yield (%)		
	25°C	35°C	50°C
20	40.3	43.2	25.8
50	48.6	46.4	26.3
100	53.0	45.0	27.5

Styrene: 16 mmol; $[Pt(C_2H_5)(CH_3SO_3)(DPPB)]$: 0.05 mmol; substrate/Pt molar ratio: 320; toluene: 20 ml; reaction time: 22 h.

data relevant to the catalytic activity of complex **2a** at various temperatures and pressures.

Some trends of the data of Table 6 resemble those of Table 4. In particular, at 25°C the catalytic activity depends on the hydrogen pressure, but not at higher temperatures. Another common feature is the decrease of the observed catalytic activity when the reaction temperature is 50°C. However, apart from the data obtained at 25°C and $P(H_2) = 20$ atm, the catalytic activity displayed by complex **2a** is always lower than that of the original system. Thus it appears that under conditions different from those of Table 5 the reaction between complex **1a** and methanesulfonic acid does not proceed quantitatively to form complex **2a**. Accordingly, the ^{31}P-NMR spectra of the solutions recovered at the end of the catalytic experiments display complex patterns we have been unable to assign.

3. Conclusions

This study shows that the system formed by complex **1a** and 1 equivalent of CH_3SO_3H is particularly complicated since it produces different catalytic species depending on the hydrogen pressure and reaction temperature. Consequently, the observed catalytic activity is likely to be due to several different systems.

We have proved the involvement of complexes **2b** and **3** in the catalytic process at 25°C and $P(H_2)$ 20 atm, but at higher temperatures and pressures other species such as $[PtH_2(DPPB)]$ [8], which is the synthetic precursor of complex **1a**, are likely to be formed. In fact, complexes $[Pt(C_2H_4)\{Cy_2P(CH_2)_nPCy_2\}]$ (n = 2–4) can be converted into the corresponding *cis*-dihydride species $[PtH_2\{Cy_2P(CH_2)_nPCy_2\}]$ in the presence of H_2 [22]. These last complexes have been reported to be active in the hydrogenation of olefins [23]. Alternatively, the dihydrido-complex $[PtH_2(DPPB)]$ may be the starting species for the formation of polynuclear hydrido species. Several examples are known [24].

4. Experimental section

All reactions were performed under dinitrogen and the products were worked up in air. GLC analyses were carried out with a Hewlett-Packard HP 5890 gas chromatograph. ^1H- and ^{31}P-NMR spectra were recorded on Bruker AC 200 or on Varian VXR 400 spectrometers in $CDCl_3$ or in CD_2Cl_2. Elemental analyses were performed by the Department of Organic Chemistry of the University of Florence. Methanesulfonic acid (Aldrich) was distilled before use. $[Pt(C_2H_4)(DPPB)]$ [8] was synthesised as described in the literature.

4.1. Hydrogenation experiments

The hydrogenation apparatus consists of a homemade 150 ml stainless steel autoclave equipped with valves and manometer. In a typical experiment, styrene (16 mmol) was placed in a 150 ml autoclave together with toluene (20 ml), $[Pt(C_2H_4(DPPB)]$ (0.05 mmol) and methanesulfonic acid (0.05 mmol) and the reaction mixture magnetically stirred. The reactor was pressurised to the chosen pressure and heated to the desired reaction temperature in a thermostated bath (±0.1°C). After 22 h, the reactor was cooled to room temperature, the residual gas removed, and the reaction mixture analysed by GLC. Hydrogenation experiments carried out at different stirring rates give reproducible results thus excluding transport phenomena influences on the reaction rate.

4.2. Preparation of transition metal complexes

4.2.1. $[Pt(C_8H_8)(DPPB)]$ (1b)

$[Pt(C_2H_4)(DPPB)]$ (0.32 g, 0.5 mmol) was added to a dichloromethane solution (10 ml) of styrene (0.22 g, 2 mmol). The resulting yellow solution was stirred for 5 h, then concentrated under reduced pressure, and hexane was added. The resulting yellow solution was stored at 4°C overnight to give the product as a pale yellow powder which was filtered off, washed with cold hexane and dried *in vacuo*. Yield 0.11 g, (30%). Anal: Calcd. for $C_{36}H_{36}P_2Pt$: C, 59.58; H, 5.00. Found: C, 59.01; H, 4.93%.

4.2.2. $[Pt(C_2H_5)(CH_3SO_3)(DPPB)]$ (2a)

Methanesulfonic acid (125 μl, 1.93 mmol) was added to a cold (0°C) suspension of $[Pt(C_2H_4)(DPPB)]$ (1.13 g, 1.74 mmol) in diethyl ether (30 ml). After stirring 3 h, the suspension was filtered to give a white solid which was washed with ether and dried *in vacuo*. Yield: 1.09 g (83%). Anal: Calcd. for $C_{31}H_{36}O_3P_2PtS$: C, 49.93; H, 4.87. Found: C, 49.88; H, 4.78%.

4.2.3. $\{Pt[CH(CH_3)(C_6H_5)](CH_3SO_3)(DPPB)\}$ (2b)

$[Pt(C_2H_4)(DPPB)]$ (0.45 g, 0.70 mmol) was added to a dichloromethane solution (5 ml) of styrene (0.44 g, 4 mmol). The resulting yellow solution was stirred for 2 h, then methanesulfonic acid (45 μl, 0.69 mmol) was added and the mixture was stirred for 1 h. Addition of diethyl ether precipitated the product as an pale yellow powder, which was washed with hexane and dried *in vacuo*. Yield 0.18 g, (32%). Anal: Calcd. for $C_{37}H_{40}O_3P_2PtS$: C, 54.08; H, 4.91. Found: C, 53.25; H, 5.00%.

4.2.4. $[Pt(H_2O)_2(DPPB)(CH_3SO_3)_2]$ (3)

Methanesulfonic acid (100 μl, 1.54 mmol) was added to a cold (0°C) dichloromethane solution (20 ml) of

[Pt(C_2H_4)(DPPB)] (0.55 g, 0.73 mmol). After stirring overnight, the solution was concentrated under reduced pressure. Addition of diethyl ether gave the product as an off-white powder, which was washed with ether, hexane and dried *in vacuo*. Yield 0.52 g, (85%). Anal: Calcd. for $C_{30}H_{38}O_8P_2PtS_2$: C, 42.50; H, 4.52. Found: C, 42.21; H, 4.53%.

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