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Pt^0-complexes as catalyst precursors for homogeneous carbon–carbon and carbon–oxygen double bond hydrogenation

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Abstract

Complexes of the type $Pt(C_2H_4)$ (chelating diphosphine) in the presence of methanesulfonic acid have been found to be active catalysts for the hydrogenation of carbon–carbon and carbon–oxygen double bonds. The terminal olefin reduction is accompanied by extensive substrate isomerization, and the resulting internal alkenes undergo very little hydrogenation. The highest catalyst activity is displayed in the hydrogenation of olefinic substrates bearing an electron-withdrawing group. The catalytic system is also active in the hydrogenation of aldehydes to the corresponding alcohols, whereas it is almost inactive in hydrogenation of ketones. The results obtained in the asymmetric hydrogenation of prochiral olefinic substrates allow formulation of a possible intermediate in the catalytic cycle.

Introduction

It is well-known that a combination of Pt^{II} species and Sn^{II} halides provide systems active in the catalytic hydrogenation of carbon–carbon double bond [1–5]. On the other hand, there are very few reports of the use of Pt^{II} complexes as hydrogenation catalysts in the absence of Sn^{II} promoters [6–8] and, to our knowledge, only one paper deals with hydrogenation of olefins catalysed by Pt^0 mononuclear complexes [9].

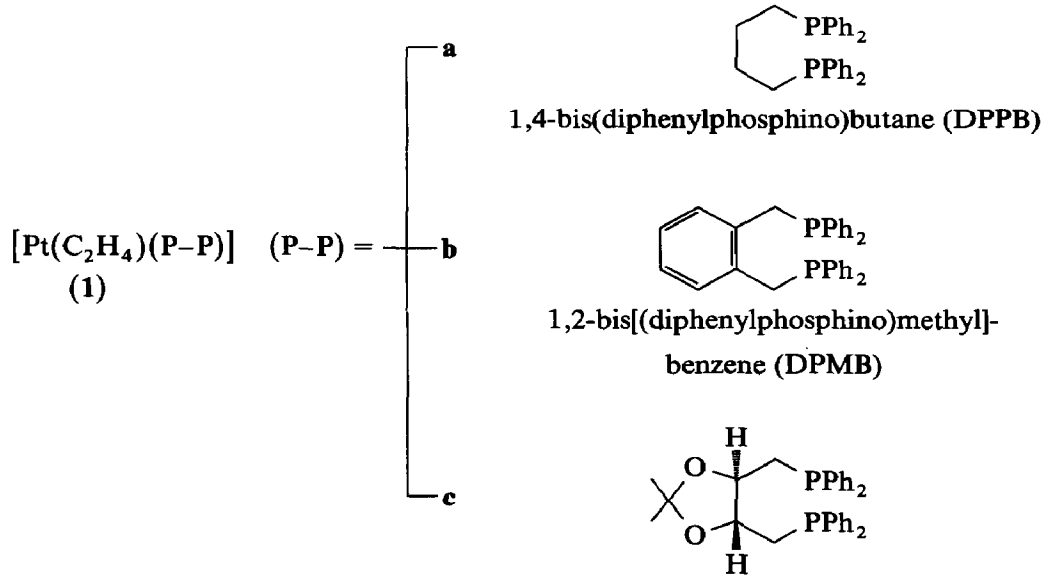
Reduction of aldehydes catalysed by platinum clusters has been described [10], but no active mononuclear species have been previously reported.

Recently we showed that Pt^0-olefin complexes of the type [Pt(ethylene) (chelating diphosphine)] in the presence of CH_3SO_3H are active catalysts in styrene hydroformylation [11]. In this latter case the "oxo" reaction is accompanied by some substrate hydrogenation and partial reduction of the aldehydes to the corresponding alcohols. These observations prompted us to investigate the activity of these systems in hydrogenation of carbon–carbon and carbon–oxygen double bonds.

Results

The catalytic systems were prepared by adding one equivalent of CH_3SO_3H to toluene solutions of complexes $[Pt(C_2H_4)(P-P)]$ **1a–1c**.

Table 1 presents the data for carbon-carbon double bond hydrogenation carried out in the presence of complex **1a**. The hydrogenation of 1-hexene at 80 °C and H_2 at 50 atm gave n-hexane in 29.3% yield after 22 h. This hydrogenation was accompanied by extensive substrate isomerization to give a 68.8% yield of internal hexenes (run 1). The isomerization is much faster than the hydrogenation. Thus



Scheme 1

Table 1

Homogeneous catalytic hydrogenation of carbon–carbon double bonds in various substrates [a]

Run	Substrate	Time (h)	Hydrogenation yield (%)	Hydrogenation product
1	1-Hexene	22	29.3 [b]	n-Hexane
2	Cyclohexene	22	7.9	Cyclohexane
3	3,3-Dimethyl-1-butene	22	60.6	3,3-Dimethylbutane
4	Styrene	22	95.3	Ethylbenzene
5	3-Buten-2-one	4	85.4	Butan-2-one
6	2-Cyclohexen-1-one	1	88.0	Cyclohexanone
7	Benzalacetone	22	22.7	Benzylacetone
8	Benzalacetophenone	22	23.4	1,3-Diphenylpropan-1-one
9	Cinnamic acid	22	37.5	3-Phenylpropanoic acid
10	Methylcinnamate	22	11.8	3-Phenylmethylpropanoate

[a] Cat. = **1a**/CH_3SO_3H; substrate: 16 mmol; substrate/Pt: 320; Pt/CH_3SO_3H: 1; toluene: 20 ml; temperature: 80 °C; $P(H_2)$: 50 atm. [b] Isomerized hexenes were also present (68.8% yield).

Table 2

Homogeneous catalytic hydrogenation of carbon–oxygen double bonds in various substrates [a]

Run	Substrate	Time (h)	Hydrogenation yield (%)	Hydrogenation product
1	Butan-2-one	22	0	–
2	Benzophenone	22	0	–
3	Cyclohexanone	22	15.8	Cyclohexanol
4	Benzaldehyde	22	84.4	Benzyl alcohol
5	Cyclohexanecarboxaldehyde	22	72.8	Cyclohexylmethanol
6	1-Heptaldehyde	22	56.5 [b]	1-Heptanol

[a] Cat. = **1a**/CH_3SO_3H; substrate: 16 mmol; substrate/Pt: 320; Pt/CH_3SO_3H: 1; toluene: 20 ml; temperature: 80 °C; P(H_2): 50 atm. [b] High boiling products were also present (19.5% yield).

under the same conditions a hydrogenation experiment (not reported in Table 1) gave 21.5% of n-hexane and 75.3% of internal hexenes along with 3.2% of unreacted 1-hexene after 4 h. Comparison of the results from these two experiments reveals that our catalytic system exhibits low activity towards internal olefins. This was confirmed by hydrogenation of cyclohexene which yielded only 8% of cyclohexane after 22 h (run 2).

In the presence of non isomerizing α-olefins such as 3,3-dimethyl-1-butene and styrene the hydrogenation is considerably faster (runs 3 and 4). The presence of the phenyl group allowed the hydrogenation of the conjugated carbon–carbon double bond to be carried out under milder conditions; thus it was possible to hydrogenate styrene at room temperature and H_2 at 20 atm with 36.7% yield after 19 h (see run 2 of Table 4). The hydrogenation of α,β-unsaturated ketones such as 3-buten-2-one and 2-cyclohexen-1-one confirmed that the presence of an electron-withdrawing group increases the activity of the carbon–carbon double bond (runs 5 and 6). The data for runs 7–10 show that the presence of two electron-withdrawing groups on the substrate lowers the hydrogenation rate.

Table 2 reports the results of the catalytic hydrogenation of carbon–oxygen double bonds promoted by complex **1a** under the conditions used for the olefin hydrogenation. The catalytic system showed low or no activity in hydrogenation of ketones: only cyclohexanone was reduced, to give cyclohexanol in 15.8% yield after 22 h (run 3). In contrast, the system is much more effective in the hydrogenation of aldehydes (runs 4–6). In the hydrogenation of 1-heptanal we also observed the formation of high boiling products (~ 20% yield) arising from condensation reactions, probably promoted by the acid cocatalyst.

In Table 3 are shown the results of preliminary studies of hydrogenation of some representative substrates carried out at various CH_3SO_3H/Pt molar ratios. A three-fold excess of the acid enhances the catalyst activity in carbon–carbon double bond hydrogenation. At very high CH_3SO_3H/Pt ratios (run 3) this positive effect is less marked. The presence of an excess of cocatalyst also enhances the rate of reduction of the carbon-oxygen double bond (runs 8 and 9).

The effect of the nature of the diphosphine ligand was examined in the experiments giving rise to Table 4. The data indicate that the catalytic activity depends on the nature of the phosphine ligand–organic substrate combination. The comparison of runs 1–3 shows that in hydrogenation of styrene the catalyst efficiency decreases

Table 3

Influence of the CH_3SO_3H concentration on the hydrogenation of various substrates [a]

Run	Substrate	Pt/CH_3SO_3H (molar ratio)	Time (h)	Hydrogenation yield (%)	Hydrogenation product
1	Cyclohexene	1/1	22	7.9	Cyclohexane
2	Cyclohexene	1/3	8	52.2	Cyclohexane
3	Cyclohexene	1/12.5	8	30.6	Cyclohexane
4	Benzalacetophenone	1/1	22	23.4	1,3-Diphenylpropan-1-one
5	Benzalacetophenone	1/3	22	100.0	1,3-Diphenylpropan-1-one
6	Tiglic acid [b]	1/1	22	<1	2-Methylbutanoic acid
7	Tiglic acid [b]	1/3	22	10.0	2-Methylbutanoic acid
8	Cyclohexanone	1/1	22	15.8	Cyclohexanol
9	Cyclohexanone	1/3	22	47.6	Cyclohexanol

[a] Cat. = **1a**/CH_3SO_3H; substrate: 16 mmol; substrate/Pt: 320; toluene: 20 ml; temperature: 80 °C; $P(H_2)$: 50 atm. [b] Experiment carried out in the presence of **1c**/CH_3SO_3H.

Table 4

Homogeneous catalytic hydrogenation of various substrates in the presence of platinum(0) precursors containing different diphosphine ligands [a]

Run	Substrate	Ligand (P–P) [b]	Time (h)	T (°C)	$P(H_2)$ (atm)	Hydrogenation yield (%)	Hydrogenation product
1	Styrene	**c**	19	25	20	66.0	Ethylbenzene
2	Styrene	**a**	19	25	20	36.7	Ethylbenzene
3	Styrene	**b**	19	25	20	22.0	Ethylbenzene
4	2-Cyclohexen-1-one	**a**	4	80	50	100.0 [c]	Cyclohexanone
5	2-Cyclohexen-1-one	**b**	4	80	50	60.5	Cyclohexanone
6	Benzaldehyde	**a**	22	80	50	84.4	Benzyl alcohol
7	Benzaldehyde	**b**	22	80	50	100.0	Benzyl alcohol
8	Cyclohexanone	**a**	22	80	50	15.8	Cyclohexanol
9	Cyclohexanone	**b**	22	80	50	5.2	Cyclohexanol

[a] Cat. = $Pt(C_2H_4)(\widehat{P-P})/CH_3SO_3H(1/1)$; substrate: 16 mmol; substrate/Pt: 320; toluene: 20 ml. [b] See Scheme 1. [c] Cyclohexanol is also present (1.3% yield).

Table 5

Homogeneous asymmetric carbon–carbon double bond hydrogenation of prochiral substrates [a]

Run	Substrate	Catalyst precursor	Time (h)	T (°C)	$P(H_2)$ (atm)	Hydrogenation yield (%)	O.P. (%)	Config.
1	α-Ethylstyrene	**1c**/CH_3SO_3H (1/1)	19	25	20	18.0	8.0 [b]	(−)-*R*
2	α-Ethylstyrene	**1c**/CH_3SO_3H (1/3)	19	80	50	38.5	5.5 [b]	(−)-*R*
3	α-Ethylstyrene	**1a**/R^*SO_3H (1/1)	40	80	50	29.4	0.7 [b]	(−)-*R*
4	Tiglic acid	**1c**/CH_3SO_3H (1/3)	22	80	50	10.0	0	

[a] Substrate: 16 mmol; substrate/Pt: 320; toluene: 20 ml. R^*SO_3H = (+)-10-camphorsulfonic acid monohydrate. [b] Determined taking for optically pure (+)-(*S*)-2-phenylbutane $[\alpha]^{25}_{D\,max} = 29.3$ [12], (ρ = 0.858) [13].

in the series **1c** > **1a** > **1b**. Furthermore, in the hydrogenation of 2-cyclohexen-1-one and cyclohexanone **1a** is again more effective than **1b**. Of all the substrates tested, only benzaldehyde is more readily reduced in the presence of **1b**.

The catalytic system was tested also in the asymmetric hydrogenation of prochiral olefinic substrates. The results obtained in the presence of the chiral complex **1c** are summarized in Table 5. Whereas tiglic acid was reduced with no asymmetric induction, α-ethylstyrene was hydrogenated to (−)-(*R*)-2-phenylbutane with moderate optical purity (runs 1 and 2). In our opinion the most significant result is the low but measurable asymmetric induction obtained in the hydrogenation of α-ethylstyrene in the presence of a catalytic system prepared by adding the chiral promoter (+)-10-camphorsulfonic acid to complex **1a**, which has no chiral centers on the phosphorus ligand (run 3).

Discussion

In many respects our catalytic system displays features similar to those provided by some Pt^{II} species in the presence of Sn^{II} and, in particular, by the system $[PtCl_2(PPh_3)_2]/SnCl_2$ [1,2]. All these systems display the highest activity in α-olefins hydrogenation, although this reaction may be accompanied by extensive substrate isomerization. On the other hand, these systems are less effective in the reduction of internal double bonds (including those in cyclic olefins), probably owing to steric effects. A common feature is the enhancement of the ease of the hydrogenation of substrates bearing one electron-withdrawing group [2]. Many homogeneous transition-metal-based catalytic systems display this effect which may be ascribed to electronic factors which either favour the coordination of the substrate to the metal or, by lowering the electron density in the double bond make it more susceptible to nucleophilic attack by hydrido ligand [14]. Conversely, alkenes bearing two electron-withdrawing groups are hardly hydrogenated probably because of an unfavourable combination of electronic and steric effects.

It is noteworthy that our catalytic system is more versatile than other platinum-based hydrogenation catalysts, since it can promote the reduction of carbon–oxygen double bonds. To the best of our knowledge this is the first example of a mononuclear platinum complex active in such a reduction.

It is also relevant to note that this system can also be used in the asymmetric reduction of prochiral olefins, since only a few examples of asymmetric hydrogenations promoted by platinum complexes have been described [15].

Some insights into the reaction mechanism are provided by the results obtained in the asymmetric hydrogenation of α-ethylstyrene. The asymmetric induction obtained in the presence of complex $[Pt(C_2H_4)((+)\text{-DIOP})]$ **1c** indicates that the substrate coordination to the metal center occurs before the alkyl formation. Moreover, since asymmetric induction is also obtained when the only chiral species present in the reaction mixture is (+)-10-camphorsulfonic acid, we can assume that the acid counterion is coordinated to the metal, at least in the step which leads to the alkyl formation. Therefore an intermediate step of the catalytic cycle may be the following reaction:

$$(P\text{–}P)PtHX(olefin) \rightarrow (P\text{–}P)Pt(alkyl)X \quad (X = OSO_2R)$$

The alkyl complex [Pt(alkyl)X(P–P)] could be formed in the first catalytic cycle by the reaction sequence described below:

$$(P–P)Pt(C_2H_4) + \text{olefin} \rightarrow (P–P)Pt(\text{olefin}) + C_2H_4$$

$$(P–P)Pt(\text{olefin}) + HX \rightarrow (P–P)Pt(\text{alkyl})X$$

It is known that ethylene bonded to a Pt^0 metal center can be readily replaced by other olefinic ligands, especially if they bear electron-withdrawing groups [9], this reaction is favoured by the high concentration of the entering olefin. Finally the reaction of Pt^0-olefin complexes with electrophilic reagents such as HX to give the corresponding Pt^{II}-alkyl derivative is well-documented [16–18].

The most outstanding steps of the reaction mechanism are those involved in the hydrogen activation and product formation, especially as far as the role played by the excess of organic acid is concerned. Further studies are necessary, however, to gain deeper insight into this topic.

Probably aldehydes and ketones are hydrogenated by an analogous mechanism. Indeed, these substrates can undergo electrophilic attack by acid species [19] when coordinated to a low valent metal center. A pertinent example in platinum chemistry has been reported by Head [20].

Conclusions

Our catalytic system is versatile and, owing to its different activity towards various substrates, it is suitable for use in selective hydrogenation of species bearing two or more reducible functional groups. In this connection the possibility of tuning the performances of our catalytic system by modifying various parameters such as the reaction conditions, the diphosphine ligand, the platinum to cocatalyst molar ratio, and the strength of the cocatalyst acid, holds out much promise. Elucidation of the reaction mechanism remains a major objective.

Experimental

GLC analyses were carried out on a Carlo Erba HRGC 5300 or on a Hewlett Packard HP 5890 gas chromatograph. Optical rotations were measured with a Perkin Elmer 241 polarimeter using a 1 dm tube.

The identification of the hydrogenation products was accomplished by comparison of their GLC retention times and NMR and IR spectra with those of authentic samples.

Benzalacetone and cinnamic acid were purchased from Janssen Chimica and were used as received. Benzalacetophenone, tiglic acid and methyl cinnamate were used as received from Fluka A.G. α-Ethylstyrene was prepared as previously described [21]. All the other substrates were distilled before use. Methanesulfonic acid was used as received from Janssen Chimica and *d*-10-camphorsulfonic acid monohydrate as received from C. Erba Analyticals. (+)-DIOP and DPPB (Strem Chemicals) were used as received, and DPMB was prepared as previously described [18]. The catalyst precursors $[Pt(C_2H_4)(DPPB)]$ [17], $[Pt(C_2H_4)(DPMB)]$ [18] and $[Pt(C_2H_4)((+)\text{-DIOP})]$ [16] were made by published procedures.

Solvents were purified by standard methods [22].

Hydrogenation reaction procedures

The catalytic hydrogenations were carried out in a 150 ml stainless steel autoclave. In a typical experiment the autoclave was charged under nitrogen with 0.05 mmol of the platinum catalyst, a solution of 16 mmol of the substrate in 20 ml of anhydrous toluene, and 0.05 mmol of methanesulfonic acid. The reactor was pressurized to 50 atm with H_2 at room temperature, and heated with stirring at 80 °C (±0.5 °C); after the chosen reaction time it was cooled at room temperature and the residual gas vented off. The reaction mixture was analyzed by GLC to determine the extent of conversion and the selectivity of the reaction.

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