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ACTIVATION OF H_2 WITH ALLYLPALLADIUM(II) DERIVATIVES. SELECTIVE CATALYTIC HYDROGENATION OF ALLENE TO PROPENE

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Summary

The behaviour of allylpalladium(II) complexes in THF towards molecular hydrogen under mild experimental conditions has been studied. The decomposition to palladium metal and propane is discussed in terms of the fluxionality of the allyl moiety and the stability of a proposed Pd—H intermediate. Reaction of allylpalladium(II) complexes with H_2 and allene results in catalytic selective hydrogenation to give propene.

Introduction

The *syn—anti* interconversion of allylic protons in neutral η^3-allyl-platinum(II) and -palladium(II) complexes is well known to occur via the formation of a η^1-allyl intermediate [1—4]. These 14-electron species can be regarded as potentially useful for catalytic purposes because of the vacant coordination site and allylic complexes are known to undergo some of the basic reaction involved in catalytic processes such as insertion of CO [5], olefins, or acetylenes [6], and nucleophilic attack [7] on the coordinated allylic group.

Reaction of allylpalladium complexes with molecular hydrogen has been reported to give palladium metal [8,9], with evolution of alkene, which can be eventually completely hydrogenated, but a satisfactory mechanism for this reaction has not been proposed. The usual oxidative addition of H_2 to d^8 complexes is unlikely to apply with palladium(II), which is rarely involved in this type of reaction; furthermore palladium hydride derivatives are rather uncommon and unstable even in the palladium(II) oxidation state [10—16].

However, in recent times the reaction of allyl palladium(II) complexes with molecular hydrogen has been employed in the preparation of dispersed-metal heterogeneous catalysts [9,17]. We have thus examined the reactions of allylpalladium(II) complexes with molecular hydrogen in order to: (i) get more information about the elementary steps involved in the reduction reaction to palladium metal; (ii) test possible catalytic implications; (iii) study the influence of the $\eta^3 \rightleftharpoons \eta^1$ interconversion with respect to H_2 activation.

Results and discussion

When a solution of $[(C_3H_5)Pd(PPh_3)Cl]$ (I) in THF is treated with molecular hydrogen at atmospheric pressure, decomposition to palladium metal occurs in 4 h. A GLC analysis of the gas phase shows an initial evolution of propene, which is rapidly hydrogenated to propane as palladium metal is produced. After the reaction is completed, added propene is found to undergo hydrogenation, proving the effectiveness as hydrogenation catalyst of the palladium metal obtained by this route. Thus the consecutive reactions 1 and 2 are responsible

(1)

$$\text{propene} + H_2 \xrightarrow{\text{palladium metal}} \text{propane} \quad (2)$$

for the conversion of the allylic moiety to propane.

In reaction 1, the interaction of H_2 with allylic and chloride ligands, coordinated to the metal center suggests the formation of a labile Pd—H species at some stage of the reaction; such species have been often invoked in processes leading to the formation of palladium metal [18]. Reaction 1 can be regarded as an overall palladium(II) → palladium(0) reductive elimination.

We found that by using ligands which are particularly able to stabilize zerovalent palladium, the formation of palladium metal can be avoided. Thus, $\{(C_3H_5)Pd[P(C_6H_{11})_3]_2\}^+$ reacts with H_2 under mild conditions to give propene and $\{Pd[P(C_6H_{11})_3]_2\}$, according to reaction 3.

$$\{(C_3H_5)Pd[P(C_6H_{11})_3]_2\}^+ + H_2 + NEt_3 \rightarrow \{Pd[P(C_6H_{11})_3]_2\} + C_3H_6 + HNEt_3^+ \quad (3)$$

Propene was found in the gas phase, and $\{Pd[P(C_6H_{11})_3]_2\}$ was identified by its ^{31}P NMR spectrum (singlet at δ 38.7 ppm) [19] and by comparison with authentic sample [7a].

The behaviour of (η^3-allyl)palladium(II) derivatives towards molecular hydrogen was found strongly dependent on the type of complex used. Apart from the peculiarity of $\{(C_3H_5)Pd[P(C_6H_{11})_3]_2\}^+$, we observed that $[Pd(C_3H_5)_2]$ decomposes instantaneously to palladium metal both in solution and in the solid state, whereas I takes about 4 h in THF solution, while [(1-methylallyl)-$Pd(PPh_3)Cl$] (II) and [(2-methylallyl)$Pd(PPh_3)Cl$] (III) are stable under the same conditions over a much longer period of time (see Table 1). This sequence of increasing stability parallels the decrease in the fluxionality of the coordinated allylic moiety.

The ease of fluxionality is indicated by the dynamicity for the *syn—anti* interconversion of allyl protons in the NMR spectrum. In Table 1 the time necessary

TABLE 1

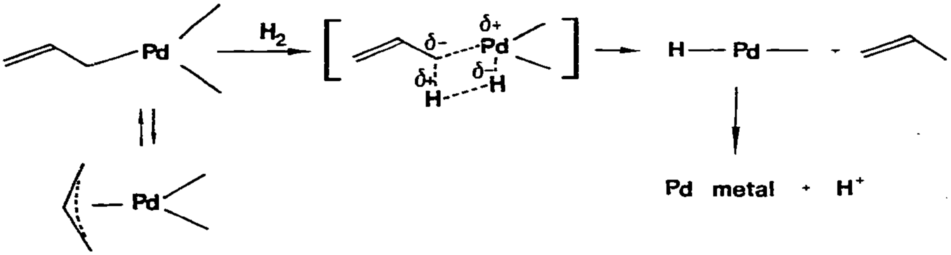
DECOMPOSITION TIME AND MAXIMUM ESTIMATED TEMPERATURE AT WHICH *syn—anti* PROTONS EXCHANGE CANNOT BE OBSERVED FOR VARIOUS (ALLYL)PALLADIUM(II) COMPLEXES [a]

Compound	Time (h) [b]	Temp. (°C) [c]
$[Pd(C_3H_5)_2]$	instantaneous	10 [d]
$[(C_3H_5)Pd(P\text{-}t\text{-}Bu_3)Cl]$	1.0	—10
$[(C_3H_5)Pd(PPhMe_2)Cl]$	24	30
$[(C_3H_5)Pd(PPh_3)Cl]$	4.5	5
$[(C_3H_5)Pd(1,5\text{-}C_8H_{12})]Cl$	24	>50
$[(1\text{-Me-allyl})Pd(PPh_3)Cl]$	stable	>50
$[(2\text{-Me-allyl})Pd(PPh_3)Cl]$	stable	40

[a] Line width of the peaks from 1.5 to 2.5 Hz. [b] THF solution under H_2 atmosphere. [c] Recorded at 90 MHz in $CDCl_3$ solution. [d] Quoted in ref. 20.

to decompose the palladium complexes under H_2 is compared with the estimated maximum temperature for which a static allyl configuration can be safely assumed in $CDCl_3$ solution from the NMR spectrum. Most of the complexes reported have been previously studied at various temperatures with NMR spectroscopy [2,20,21], but to provide directly comparable data we repeated the NMR measurements under a given set of experimental conditions, with the results shown in Table 1.

It is clear from Table 1 and literature data that the fluxionality observed depends both on the presence of substituents on the allylic ligand and the nature of the other ligands [22]. A more dynamic configuration implies a greater availability of a η^1 14-electron intermediate. Thus the parallelism between decomposition in the presence of H_2 and fluxionality justifies the following possible pathway for reaction of type 1:



In the proposed scheme the unsaturated character of the 14-electron intermediate overwhelms the weak coordinating ability of H_2; furthermore, because of the difficulty of oxidative addition of H_2 to palladium(II) species, heterolytic splitting is likely to be favoured.

However, there must be limitations on the relationship between the ease of decomposition and the fluxionality of the allyl moiety. Thus, we recorded NMR data in $CDCl_3$ and carried out decompositions in THF, and the allyl group fluxionality is known to be affected by the nature of the solvent. Moreover fluxionality can be invoked as a major factor, only as far as the hydrogen activation is concerned (i.e. the formation of Pd—H intermediate), whereas the reductive elimination step, leading to palladium metal, is certainly strongly influenced by the ancillary ligands coordinated to the metal, which have different effects on the stability of the Pd—H bond.

In view of possible catalytic implications, reaction 1 was studied in the presence of allene. It is well known that allene inserts into M—C (M = Pd, Pt) [23—25] and dienes on M—H (M = Pd, Pt) [26,27] bonds to give η^3-allylic complexes, and so on the basis of the mechanism proposed for the decomposition reaction, a scheme for catalytic hydrogenation of allene to propene can be devised.

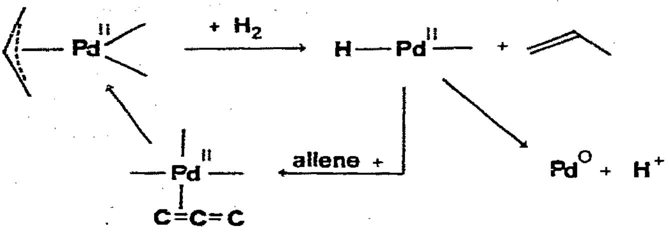
When $[(C_3H_5)Pd(PPh_3)Cl]$ is treated with an equimolecular mixture of H_2 and allene in a gas-uptake apparatus, gas absorption is observed without parallel formation of palladium metal. On monitoring the gas phase composition as the uptake proceeds, selective catalytic hydrogenation of allene to propene is detected. A 5.0×10^{-2} *M* solution in THF of I gives a molar turnover number of 20 in 4 days, at 1 atm total pressure (H_2/allene = 1) and 15°C. This confirms the formation of a palladium hydride species in the reaction of type [1].

In the catalytic reaction 4 an allene/H_2 molar ratio = 1 must be used, other-

$$\text{allene} + H_2 \xrightarrow[\text{THF, } 15^\circ\text{C}]{[(C_3H_5)Pd(PPh_3)Cl]} \text{propene} \qquad (4)$$

wise, by the end of the catalytic reaction, when the concentration of allene in solution becomes too low, the excess of hydrogen present produces Pd metal, and eventually propane, via reactions 1 and 2.

A general reaction scheme, accounting for both the H_2 activation and the hydrogenation of allene, can be written as follows:



Use of various allylpalladium(II) compounds as catalysts in reaction 4 leads to varying activities (see Table 2).

The almost similar activities found for I—III corroborate the scheme of catalysis proposed, since the same palladium hydride intermediate is operative once the initially coordinated allylic moiety is displaced. Significantly, when II and III are used, 1-butene and isobutene, respectively, can be detected in the gas phase. On the other hand the marked difference between $[Pd(C_3H_5)_2]$ and the other compounds is certainly due to the different rates of decomposition; in particular the absence of phosphine ligands can reduce the stability of the palladium hydride formed in the course of the reaction. As for fluxionality the validity of the scale reported in Table 1 is somewhat dubious under the conditions of the catalytic reaction, where not only is the solvent different from that used for the NMR spectra, but allene and H_2 are simultaneously present in solution (in agreement with the findings of Hughes and Powell [24]).

In contrast to previous reports [24], we did not observe insertion of allene into the allyl—palladium bond; after the catalytic run, no organic insertion product can be found in solution, and the catalyst can be recovered unchanged.

TABLE 2

CATALYTIC ACTIVITY OF (ALLYL)PALLADIUM(II) COMPLEXES IN THE HYDROGENATION OF ALLENE TO PROPENE [a]

Compound	Molar turnover number	Time (h)
$[Pd(C_3H_5)_2]$	75	1 [b]
$[(C_3H_5)Pd(P\text{-}t\text{-}Bu_3)Cl]$	46	18
$[(C_3H_5)Pd(PPhMe_2)Cl]$	19	18
$[(C_3H_5)Pd(PPh_3)Cl]$	20	96
$[(1\text{-Me-allyl})Pd(PPh_3)Cl]$	22	96
$[(2\text{-Me-allyl})Pd(PPh_3)Cl]$	18	96

[a] Allene/H_2 = 1; 1 atm total pressure; 15°C. [b] 0°C.

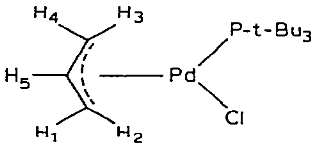
Experimental

^1H NMR spectra were recorded in $CDCl_3$ on a Varian EM390, 90 MHz spectrometer with TMS as internal standard. ^{31}P NMR spectra were recorded with a Bruker WP-60 spectrometer operating at 24.28 MHz, in Fourier transform mode, with ^1H decoupling, with 85% H_3PO_4 as external standard. GLC analysis was performed with a HP 5730 Gas Chromatograph equipped with a HP 3380A integrator. A 6 feet silica gel column thermostatted at 50°C was used during the GLC analyses.

Materials. Solvents were dried by standard methods [28] and distilled before use. Allylpalladium(II) derivatives were prepared by the routes described [2,20,21] and only the preparation of the new complex with phosphine = P(t-butyl)$_3$ is given in detail. P(t-butyl)$_3$ was synthesized by the known method [29].

Preparation of $[(C_3H_5)Pd(P(t\text{-}butyl)_3)Cl]$. To a stirred CH_2Cl_2 solution of $[Pd(C_3H_5)Cl]_2$ (368 mg, 1.0 mmol) an ether solution of the phosphine (404 mg, 2.0 mmol) was added dropwise at −10°C under nitrogen. The solution was kept at 0°C for 2 h, then concentrated under reduced pressure. On diluting with hexane the product was obtained in virtually quantitative yield. Elemental analysis: found: C, 46.3; H, 8.6; Cl, 9.1. $C_{15}H_{32}ClPPd$ calcd.: C, 46.75; H, 8.38; Cl, 9.20%. $\nu(PdCl)$ (nujol mull) 270 cm^{-1}. NMR data at −10°C: phosphine protons resonance at τ 8.53 ppm, $J(P-H)$ 11 Hz. Allylic protons resonances (J values are in Hz):

τ_1	τ_2	τ_3	τ_4	τ_5
5.34	6.23	7.23	5.90	4.66
J_{1-5} 6	J_{2-5} 12	J_{3-5} 12	J_{4-5} 6	
J_{1-P} 5	J_{2-P} 8			



Coalescence of protons 3 and 4 to a singlet centered at τ 6.56 was found at 45°C in $CDCl_3$ solution.

Reaction of $[(C_3H_5)Pd(PPh_3)Cl]$ with molecular H_2. 10 ml of a 5.0 × 10^{-2} M THF solution of the complex was evacuated and kept under H_2 in a gas absorption apparatus at room temperature (15°C) and 1 atm total pressure with stirring. During the decomposition to palladium metal, the composition of the gas phase was determined by GLC. As palladium metal appears, the gas phase contains H_2 and propene, while at the end of the decomposition, H_2, propane, and traces of propene are present. The completion of the reaction was indicated by the constancy of the total amount of propane. The suspension obtained was filtered and $[HPPh_3]Cl$ was isolated from the solution. This was identified by comparison with an authentic sample (IR spectrum).

The decomposition reactions of allylpalladium(II) derivatives listed in Table 1 were carried out similarly.

Reaction of $\{(C_3H_5)Pd[P(C_6H_{11})_3]_2\}Cl$ *with molecular* H_2. A solution of $[(C_3H_5)PdCl]_2$ (184 mg, 0.5 mmol) in THF was treated under nitrogen with solid $P(C_6H_{11})_3$ (562 mg, 2.0 mmol) with stirring. After 2 h triethylamine was added (0.140 ml, 1.0 mmol). The N_2 atmosphere was replaced with H_2, and the solution set aside overnight with vigorous stirring. After this time the gas phase GLC analysis showed the presence of propene, and so the solution was taken to dryness under nitrogen. The residue was extracted with toluene and $\{Pd[P(C_6H_{11})_3]_2\}$ was obtained by adding anhydrous CH_3OH and cooling. The product was identified by comparison of its IR and NMR spectra with those of an authentic sample [19].

Hydrogenation of allene to propene catalyzed by allylpalladium(II) complexes. In a typical experiment 10 ml of a 5.0×10^{-2} *M* solution of $[(C_3H_5)Pd(PPh_3)Cl]$ in THF was evacuated and connected with a constant pressure gas absorption apparatus filled with a 1/1 mixture of allene/H_2 (1 atm total pressure). Sampling of the gas phase was performed through a side-arm fitted with a serum-cap. The progress of the reaction was monitored with GLC.

Catalytic reactions using complexes listed in Table 2, were carried out under the same conditions.

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