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Selective Hydrogenation of Dienes to Monoenes Catalyzed by (Allyl)Pd(II) Complexes

GIORGIO STRUKUL and GIOVANNI CARTURAN

Istituto di Chimica Generale, Università di Venezia, Venice, Italy and Centro di Chimica Metallorganica del C.N.R., c/o Istituto di Chimica Industriale, Università di Padova, Padua, Italy

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Hydrogenation of 1,5-COD, 1,3-COD, 1,4-octadiene and 1,7-octadiene to the corresponding monoenes has been carried out under mild conditions, using different (allyl)Pd(II) derivatives in N,N-dimethylacetamide solution. Experiments on the 1,3-COD system suggest a mechanism involving the formation of hydrido–Pd(II) species followed by insertion of diene to restore the allylic moiety. Non conjugated dienes are isomerized prior to hydrogenation. The complete selectivity appears to result from an intrinsic property due to formation of η^3*-allylic intermediates.*

Introduction

Homogeneous hydrogenation of olefins catalyzed by transition metal complexes is a thoroughly investigated reaction, whose mechanistic details vary widely for different catalysts [1].

In the endeavour to prepare highly active catalysts with increasingly better stability and utility, one of the open aspects in the field of hydrogenation is the achievement of a selective hydrogenation of dienes to monoenes [2]. Although this reaction has been known for many years, even in the better described cases [3] the reaction is the first step of a complete hydrogenation to alkanes, the selectivity arising from a relatively high ratio between the first step rate constant compared to the second, usually related to a thermodynamic selectivity in terms of stronger binding of diene compared to monoene. A complete selectivity is related to the availability of a catalyst able to hydrogenate dienes and be unreactive towards monoenes.

We recently reported the selective hydrogenation of allene to propene using (η^3-allyl)Pd(II) complexes

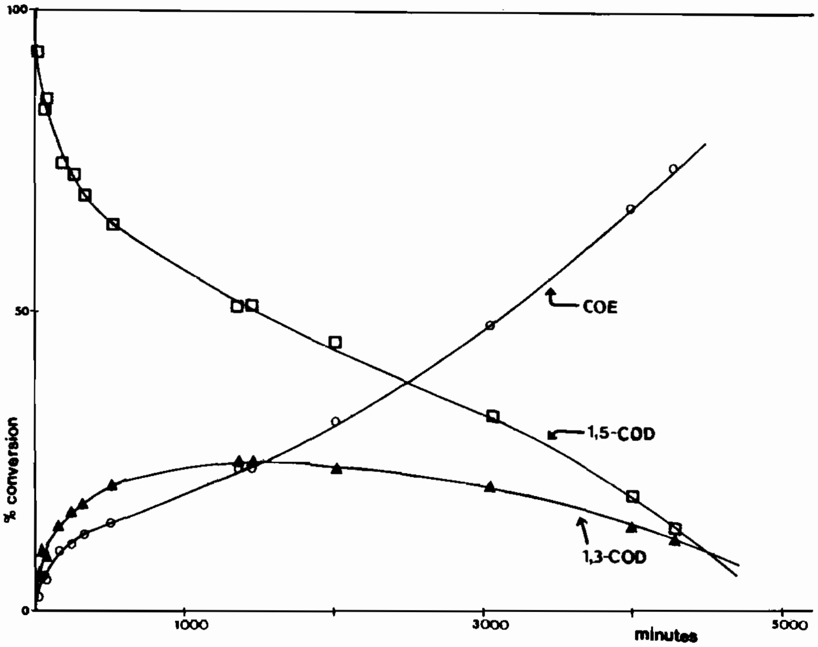


Fig. 1. Hydrogenation of 1,5-COD in the presence of (1Me-allyl)Pd(PPh$_3$)Cl. Reaction conditions: [Pd] = 2.4 × 10^{-2} M; [1,5-COD] = 7.4 × 10^{-1} M; solvent DMA; H$_2$ press. = 800 torr; T = 55 °C.

as catalysts [4]. The proposed mechanism, which involves the formation of a Pd–H species followed by insertion of allene to restore the Pd(II) coordinated allylic moiety, seems likely for any double bond olefinic systems. The formation *in situ* of Pd–H species should *per se* imply the possibility of obtaining η^3-allylic species at least from conjugated dienes [5]. This system is in principle a promising approach to the selective hydrogenation of dienes to monoenes, since only the former can give the palladium allylic intermediates reactive towards molecular hydrogen.

Results and Discussion

On treating a solution of 1,5-cyclooctadiene (1,5-COD) in N,N-dimethylacetamide (DMA) in the presence of (1Me-allyl)Pd(PPh$_3$)Cl (1), gas uptake can be detected. The hydrogenation reaction, monitored with g.l.c. analysis, shows the presence in solution of 1,3-COD and cyclooctene (COE) along with the starting 1,5-COD. The concentration profile with time of these three olefinic components in a typical experiment is shown in Fig. 1. The final gas uptake measurement gives a 1/1 ratio with the starting diene; at the end of the catalytic reaction g.l.c. analysis shows the presence of only COE. Thus compound (1) is an effective catalyst for both the selective hydrogenation of 1,5-COD to COE and the isomerization of 1,5-COD to 1,3-COD.

We previously reported [4] on the reactivity of various (allyl)Pd(II) complexes towards molecular hydrogen to give Pd metal. This decomposition reaction was recognized to occur *via* an unstable H–Pd(II) species (reactions 1 and 2), which on quenching with allene was usefully employed in the hydrogenation of the latter to propene.

$$\text{(allyl)Pd} + H_2 \rightarrow \text{olefin} + \text{H–Pd} \qquad (1)$$

$$\text{H–Pd} \rightarrow \text{Pd metal} + H^+ \qquad (2)$$

An extension of the same type of reaction pathway to the present case seems plausible (the system being different only in the olefin), at least as far as 1,3-COD is concerned. The insertion of conjugated dienes into M–H bonds (M = Ni, Pt) to form allylic species is well documented [6, 7] although this has been established only recently [5] in the case of palladium.

Attempts to hydrogenate monoolefins (for example cyclooctene, cyclohexene, 1-octene) in the presence of (1) failed, no reaction product being detected even after several days. The use of (1) as hydrogenation catalyst seems attractively limited to the conversion of dienes to monoenes, the formation of an allylic intermediate being the key step.

At the end of the hydrogenation (1) can be recovered in virtually quantitative yields (>85%). The presence of some Pd metal cannot be completely ruled out, although black palladium only becomes visible on keeping the exhausted mixture under H$_2$ for several days. When a completely hydrogenated slurry was left aside under H$_2$ for 1 week until, according to reactions [1] and [2] massive amounts of Pd metal were observed, subsequent addition of fresh 1,5-COD did not show appreciable hydrogenation activity. Moreover the UV spectra of the reaction mixture in the 500–350 nm region (featureless) before and during a typical catalytic run do not significantly differ in the extinction coef-

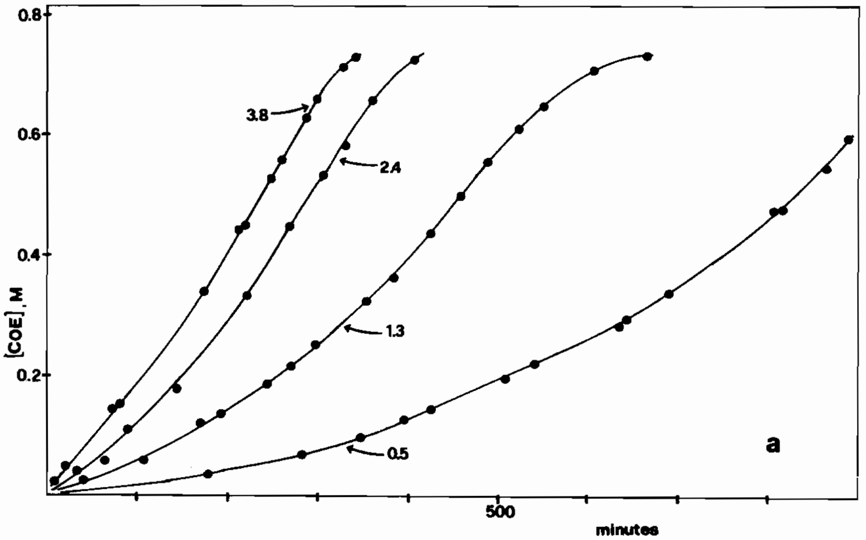


Fig. 2. A) Effect of Pd concentration on the catalytic activity. Reaction conditions: [Pd] × 10^{-2} *M* on individual plots; [1,3-COD] = 0.74 *M*; H$_2$ press. = 800 torr; solvent DMA; T = 55 °C.

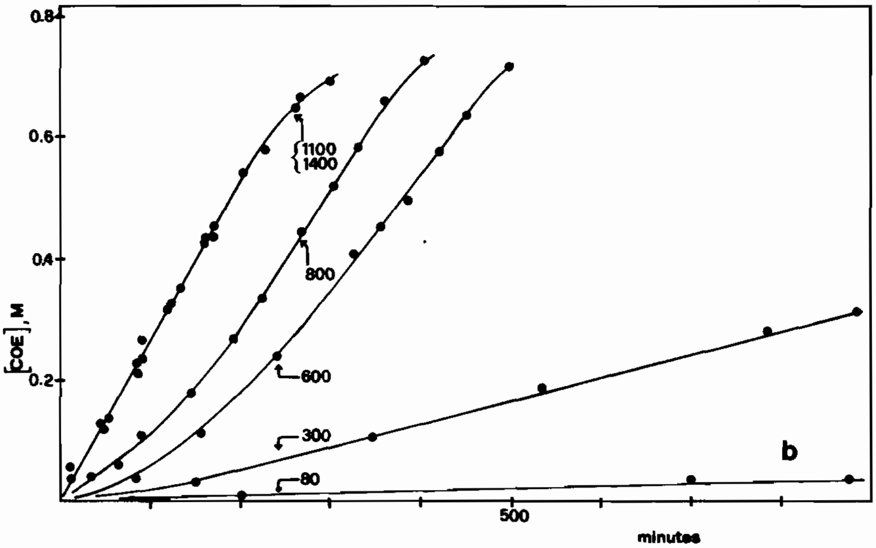


Fig. 2. B) Effect of H_2 pressure on the catalytic activity. Reaction conditions: [Pd] = 2.4 × 10^{-2} *M*; [1,3-COD] = 0.74 *M*; H_2 press. (torr) on individual plots; solvent DMA; T = 55 °C.

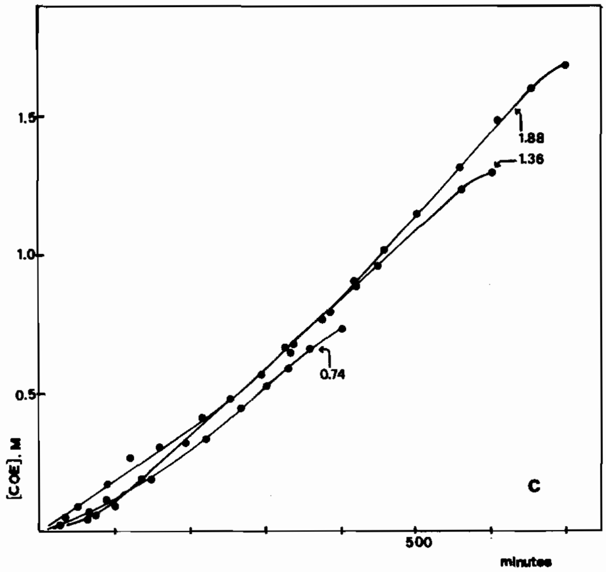


Fig. 2. C) Effect of diene concentration on the catalytic activity. Reaction conditions: [Pd] = 2.4 × 10^{-2} *M*; [1,3-COD] (*M*) on individual plots; H_2 press. = 800 torr; solvent DMA; T = 55 °C.

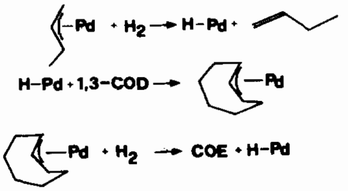
ficient. The question of whether or not the catalysis reported here is caused by traces of (colloidal) metal formed by reduction of the complex is a critical one, whenever the reaction is known to be catalyzed also by the metallic form of the central atom in the complex. Although we can offer no *absolute proof* for the homogeneity of this catalysis the observations cited above, and especially the complete inertness of the system towards monoenes, strongly support the premise that the reaction is not surface catalyzed. Furthermore for each molecule of (**1**) decomposed one molecule of PPh_3 is liberated in solution, and the poisoning effect of phosphine on Pd-metal catalyzed hydrogenations has been recently documented [8,9].

To gain better insight into the hydrogenation step, the selective hydrogenation of 1,3-COD to COE in DMA solution at 55 °C in the presence of (**1**) at constant H_2 pressure has been followed by g.l.c. analysis.

The system displays typical autocatalytic behavior [10] (Fig. 2), indicating that (**1**) is the catalyst precursor to the active species, which forms during the course of the reaction. However all attempts to identify any of the intermediate species were unsuccessful. Moreover spectroscopic investigations (IR, UV) of the reaction mixture did not yield any useful information on the nature of the intermediate species involved. Therefore the real catalyst is present in only kinetically significant amounts.

The catalytic behavior is influenced by variations in the concentration of the components of the reaction mixture and the individual effects are shown in Fig. 2. The activity increases as Pd concentration and H_2 pressure increase, and is practically not influenced by diene concentration.

A qualitative interpretation of these data suggests the following set of reactions as a possible mechanism:



(3)

(4)

(5)

Since the only Pd(II) compound that can be isolated either during the catalytic reaction or at the end of it,

TABLE I. Hydrogenation of Dienes with Various (Allyl)Pd(II) Complexes. Time Necessary to Yield 50% Conversion.

Compound	Diene	Time (min)	Pd Metal (%)[a]
$[(allyl)_2Pd]$	1,5-COD	–	90[b]
$[(allyl)Pd(PPhMe_2)Cl]$	1,5-COD	–	60
$[(allyl)Pd(1,5\text{-}COD)]BF_4$	1,5-COD	16	15
$[(allyl)Pd(PPh_3)Cl]$	1,5-COD	1200	5
$[(1Me\text{-}allyl)Pd(PPh_3)Cl]$	1,5-COD	3000	–[c]
$[(allyl)Pd(PPh_3)Cl]$	1,3-COD	180	10
$[(1Me\text{-}allyl)Pd(PPh_3)Cl]$	1,3-COD	230	–[c]
$[(1Me\text{-}allyl)Pd(PPh_3)Cl]$	1,4-octadiene	600	–[c]
$[(1Me\text{-}allyl)Pd(PPh_3)Cl]$	1,7-octadiene	550[d]	–[c]

[a] Estimated by weight at the end of the catalytic reaction. [b] Reaction performed at 0 °C. [c] Not detectable. [d] Determined with gas uptake. Reaction conditions: [Pd] = 2.4×10^{-2} *M*; [diene] = 7.4×10^{-1} *M*; solvent DMA; H_2 press. = 800 torr; T = 55 °C.

is the starting complex (1), the extent of reaction (3), within the overall process time scale, must be assumed very small compared to (4) and (5). This is supported by the relative inertness of (1) towards H_2 [4] and also by the observation that the presence of Pd metal takes several days to become visible after the hydrogenation reaction is completed.

The scheme proposed is in general agreement with the reported catalytic behavior but a rigorous mathematical treatment based even on this reductive scheme would give, at this stage, not realistically acceptable kinetic parameters.

This mechanism closely resembles the hydrogenation of conjugated dienes with $[Co(CN)_5]^{3-}$ in aqueous solution [1, 11, 12], where a complete selectivity is also found.

On this basis the observed lack of reactivity with respect to monoenes can be easily accounted for, whereas the selectivity turns out to be an intrinsic property, the allylic intermediates not being formed by monoenes.

If we now consider again the isomerization of 1,5-COD to 1,3-COD, since hydrogen is a necessary cocatalyst (no isomerization takes place in its absence) the metal hydride produced by reaction (3) must be involved; thus a metal hydride addition–elimination analogous to the general mechanism reported by Cramer and Lindsey [13], and Tolman [14] is very likely to be operative.

Significantly this isomerization reaction can be independently performed using small amounts of hydrogen to minimize hydrogenation. Thus when a 0.74 *M* solution of 1,5-COD in DMA is treated with (1) (2.4×10^{-2} *M*) in the presence of stoicheiometric amount of hydrogen (mol ratio $H_2/Pd = 1$), injected in the gas phase by means of a gas-tight syringe, only 1,3-COD is practically observed, the maximum yield obtained being 12% in 5 days, the amount of COE, owing to the very low hydrogen, being negligible (less than 1%). Therefore the complex proves a rather poor isomerization catalyst whose activity seems to be limited to double bond migration to form conjugated dienes; in fact all attempts to isomerize monoolefins such as 1-octene were unsuccessful.

In order to extend these results in a more general sense various (allyl)Pd(II) complexes were tested in the hydrogenation of 1,5-COD under the same experimental conditions of Fig. 1 (*i.e.* [Pd] = 2.4×10^{-2} *M*, [1,5-COD] = 7.4×10^{-1} *M* in DMA; H_2 press. = 800 torr; T = 55 °C). Results are reported in Table I; the time necessary to yield 50% conversion was chosen in order to have a reasonable comparison of catalytic activity even for the cases where Pd metal is produced.

The behavior found was quite dependent on the complex used; thus when using $(allyl)_2Pd$ (2) or $(allyl)Pd(PPhMe_2)Cl$ (3), very rapid, extensive decomposition to Pd metal occurs and, at least in the case of (2), the hydrogenation of 1,5-COD leads slowly to the ultimate formation of cyclooctane. On the other hand $[(allyl)Pd(1,5\text{-}COD)]^+$ (4) and $(allyl)Pd(PPh_3)Cl$ (5) display a behavior intermediate between (1) and (2) or (3). In fact selective hydrogenation with contemporary isomerization takes place even though Pd metal production is evident throughout the reaction. It is significant that, as previously reported [4], the reactivity of these (allyl)Pd(II) complexes towards H_2 to give Pd metal parallels the behavior summarized in Table I. Therefore a crucial requirement to safely achieve selective hydrogenation is that reaction (4) be conveniently fast as compared to reaction (2). This is certainly fulfilled by allene with all these complexes [4], but for the present case of 1,5-COD the choice is limited to complexes relatively unreactive towards molecular hydrogen.

Beside 1,5-COD and 1,3-COD 1,4-octadiene and 1,7-octadiene were also tested with (1). Results are reported in Table I; again the time necessary to give 50% conversion was chosen to compare the catalytic activity.

In the case of 1,4-octadiene no conjugated diene is observed during the course of the catalytic reaction. Again octenes are the final products of the overall hydrogenation reaction, present in a ratio 1-octene/2-octenes ≅ 2.

As for 1,7-octadiene, owing to the large number of possible intermediates and final products (at least 9 different components were observed during the course of the reaction) a safe attribution of the individual peaks observed in the g.l.c. analysis is almost impossible. However no octane is produced at the end.

Experimental

All chemicals were analytical grade products. Solvents were dried and distilled prior to use according to literature methods [15]; DMA was distilled over CaH_2 and stored under N_2. Olefins were passed through neutral alumina to remove peroxides, distilled and stored under N_2. All reagents for catalytic purposes were periodically checked for the presence of peroxides with the Fe^{2+}/SCN^- test. All (allyl)-Pd(II) complexes used as catalysts were prepared by already described procedures [16–20].

Hydrogenation reactions were carried out in a 25 ml round-bottomed flask equipped with a side-arm fitted with a silicone septum; two stopcocks allowed connection to the vacuum rack and a gas reservoir; temperature was maintained constant (±0.5 °C) with the aid of an oil bath; stirring was performed by a teflon coated bar driven externally by a magnetic stirrer.

A standard gas-uptake apparatus was used to determine the stoicheiometry of the reaction.

In a typical experiment the required amount of catalyst and solvent were charged into the reaction flask; the system was degassed by several freeze and thaw cycles; hydrogen was admitted into the thermostatted solution, followed by the olefin which was injected with a syringe. Progress of the reaction was monitored by periodically sampling (1 μl) the reaction mixture. Samples were injected into a Hewlett-Packard 5730A gas-chromatograph equipped with a Hewlett-Packard 3380A integrator. For the separation either 6 ft Carbowax 1500 or UCC–DMCS columns were used throughout. Products were identified with g.l.c. analysis by comparison with authentic samples and with combined g.l.c.–mass spectrometry techniques.

In the attempt to identify the intermediate species involved in the hydrogenation of 1,3-COD, a catalytic run containing 5.0×10^{-2} *M* (**1**) and 1.0 *M* 1,3-COD in DMA, was monitored. Samples taken at 50% and 95% conversion were degassed and concentrated *in vacuo*. Addition of ethyl ether gave a yellow solid that was filtered off, washed with ethyl ether and dried. In both cases the solid was found to be identical to the starting complex (**1**) (IR and NMR spectra) and was recovered in >85% yields.

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