

# Hydroxy complexes of palladium(II) and platinum(II) as catalysts for the acetalization of aldehydes and ketones

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## Abstract

The acetalization of aldehydes or ketones is a reaction of synthetic interest in organic chemistry that is commonly catalyzed by Brønsted or Lewis acids. We have found that a class of Pd(II) and Pt(II) complexes of the type  $[(P-P)M(\mu-OH)]_2^+$  ( $P-P$  = a series of diphosphines;  $M = Pd, Pt$ ) are effective catalysts for the acetalization of a variety of aldehydes and ketones in the presence of alcohols or glycols. The use of epoxides instead of alcohols resulted in lower rates and yields. The rate and yield of the reaction is not affected by the size of the diphosphine in the series dppe, dppp, dppb. Attempts to perform the reaction in a stereoselective fashion showed no difference depending on whether regular achiral catalysts or catalysts modified with chiral diphosphines were used. © 1999 Elsevier Science B.V. All rights reserved.

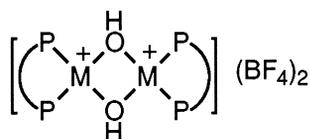
*Keywords:* Hydroxy complexes; Catalysts; Aldehydes

## 1. Introduction

The acetalization reaction is a process that is widely used in organic synthesis to protect the carbonyl group of aldehydes and ketones [1] and for the synthesis of end products (acetals), including enantiomerically pure compounds [2–7], that find practical application in the field of synthetic carbohydrate [8], steroids [9], pharmaceuticals and fragrances [10,11], and as polymers and copolymers [12]. This reaction is normally acid catalyzed, although the use of transition metal complexes as catalysts has been occasionally reported in the literature [13–17]. Recently, Gorla and Venanzi [18] observed for the first time the possibility to use cationic, solvent complexes of Rh(III), Pd(II) and Pt(II) as catalysts for the acetalization of a variety of aldehydes and ketones. According to these authors, the basic requirements necessary to achieve a high catalytic activity are the presence of an at least 2+ positive charge on the complex to ensure a sufficient Lewis acidity, and the existence of two adjacent vacant coordination sites in order to have the reactants (aldehyde/ketone and alcohol) present in a mutually *cis* position. These principles led to the design of complexes such as

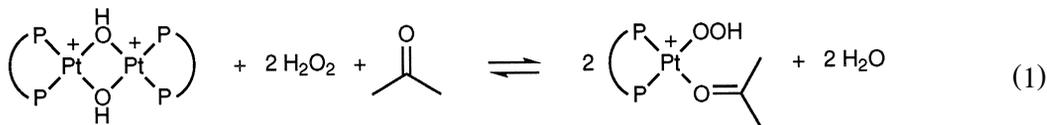
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$[(\text{dppe})\text{M}(\text{H}_2\text{O})_2]^{2+}$  ( $\text{M} = \text{Pd}, \text{Pt}$ ) that proved very active as catalysts [18]. However, these complexes are relatively unstable and, according to the mechanism of reaction suggested, they produce  $\text{H}^+$  in the system, so that acid catalysis cannot be unambiguously excluded. In this paper we report the use of a class of complexes of Pd(II) and Pt(II) shown in Chart 1, that are stable in air both in the solid state and in solution and proved also efficient catalysts for the Baeyer–Villiger oxidation of ketones with hydrogen peroxide [19]. These dimeric compounds easily react with protic molecules leading to condensation compounds in which a vacant coordination site may be present. For example, the Baeyer–Villiger oxidation of ketones with hydrogen peroxide occurs via prior bridge-splitting and condensation according to Eq. (1). Therefore, they seem particularly suited for testing as catalysts for the acetalization reaction avoiding the possible ambiguity arising from proton generation in the system.

Chart 1<sup>a</sup>

|        |   |            |   |
|--------|---|------------|---|
| M = Pd | 1 | P-P = dpmp | a |
| Pt     | 2 | dppe       | b |
|        |   | dppp       | c |
|        |   | dppb       | d |
|        |   | R-binap    | e |

<sup>a</sup> Legend: dpmp = bis(diphenylphosphino)methane; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; dppb = 1,4-bis(diphenylphosphino)butane.



## 2. Experimental section

### 2.1. Apparatus

IR spectra were taken on a Nicolet FTIR Magna 750 and on a Digilab FTS 40 interferometers either in solid (KBr pellets) or in  $\text{CH}_2\text{Cl}_2$  solution using  $\text{CaF}_2$  windows.  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AC 200 spectrometer operating in FT mode, using as external

references TMS and 85%  $\text{H}_3\text{PO}_4$ , respectively. Conductivity measurements were performed on a Radiometer instrument using  $10^{-3}$  M solutions in MeOH at 25°C. GC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. GC-MS measurements were performed on a Hewlett-Packard 5971 mass selective detector connected to a Hewlett-Packard 5890 II gas chromatograph. Identification of products was made with GC or GC-MS by comparison with authentic samples.

## 2.2. Materials

Solvents were dried and purified according to standard methods. Aldehyde and ketone substrates, alcohols, glycols and epoxides employed in the acetalization reactions were commercial products (*purum* or *puriss* quality) used without purification.

The following complexes were prepared according to literature procedures:  $[(\text{dppe})\text{Pd}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**1b**) [19],  $[(\text{dppp})\text{Pd}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**1c**) [20],  $[(\text{dppb})\text{Pd}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**1d**) [21],  $[(\text{dppm})\text{Pt}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**2a**) [22,23],  $[(\text{dppe})\text{Pt}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**2b**) [22],  $[(\text{dppp})\text{Pt}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**2c**) [22,23],  $[(\text{dppb})\text{Pt}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**2d**) [22,23],  $[(R\text{-binap})\text{Pt}(\mu\text{-OH})_2(\text{BF}_4)_2]$  (**2e**) [24].

## 2.3. $[(R\text{-binap})\text{PdCl}_2]$

The complex  $[(\text{MeCN})_2\text{PdCl}_2]$  (0.10 g, 0.38 mmol) and *R*-binap (0.24 g, 0.38 mmol) were placed solid in a round bottomed flask under nitrogen atmosphere. Dry, nitrogen saturated DCE (10 ml) were added and the orange solution was heated under reflux for 3 days. The solution was concentrated in vacuo to small volume and addition of  $\text{Et}_2\text{O}$  led to the formation of an orange precipitate, that was filtered washed several times with  $\text{Et}_2\text{O}$  and dried in vacuo (yield 91%).

Anal. Calcd. (found) for  $\text{C}_{32}\text{H}_{22}\text{P}_2\text{PdCl}_2$ : C, 59.52 (59.75); H, 3.43 (3.27). IR (KBr pellet): 303, 291  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  28.8 ppm (s).

## 2.4. $[(R\text{-binap})\text{Pd}(\mu\text{-OH})_2(\text{BF}_4)_2]$ (**1e**)

The complex  $[(R\text{-binap})\text{PdCl}_2]$  (0.24 g, 0.30 mmol) was placed in a round-bottomed flask, to which  $\text{CH}_2\text{Cl}_2$  (30 ml) and reagent grade acetone (55 ml) were added. After saturating with  $\text{N}_2$  the pale yellow solution, 0.613 ml (0.60 mmol) of a  $\text{AgBF}_4$  solution in acetone were added. The mixture was stirred in the dark for 1 h and then  $\text{AgCl}$  was filtered off. The resulting yellow solution was concentrated to small volume under reduced pressure and the addition of  $\text{Et}_2\text{O}$  resulted in the precipitation of a pale yellow solid that was filtered, washed with  $\text{Et}_2\text{O}$  and dried in vacuo (yield 87%).

Anal. Calcd. (found) for  $\text{C}_{64}\text{H}_{46}\text{O}_2\text{P}_4\text{Pd}_2\text{B}_2\text{F}_8$ : C, 56.63 (56.31); H, 3.42 (3.38). IR ( $\text{C}_2\text{H}_4\text{Cl}_2$  sln): 3590  $\text{cm}^{-1}$  (OH). IR (KBr pellet): 1101–997  $\text{cm}^{-1}$ .  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  29.3 ppm (s). Conductivity ( $10^{-3}$  M in MeOH): 173  $\Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .

## 2.5. Synthesis of acetals

Acetals used as standards for gas chromatography in the individual catalytic reactions were synthesized from the starting aldehyde/ketone (20 mmol) and the stoichiometric amount of alcohol/glycol in 25 ml DCE, to which 0.2 mmol PTSA were added under  $\text{N}_2$  with stirring. The solution containing the acetal was used for qualitative identification in the GC analysis.

## 2.6. Catalytic reactions

These were carried out in a 25 ml round-bottomed flask equipped with a stopcock for vacuum/N<sub>2</sub> operations and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature ( $\pm 0.1^\circ\text{C}$ ) was maintained by water circulation through an external jacket connected with a thermostat. For reactions carried out at temperatures  $> 25^\circ\text{C}$ , the reaction vessel was equipped with a reflux condenser and heating was ensured by a thermostatted external oil bath. Stirring was performed by a teflon-coated bar driven externally by a magnetic stirrer.

The following general procedure was followed: The required amount of catalyst was placed solid in the reactor which was evacuated and filled with N<sub>2</sub>. Nitrogen saturated alcohol/glycol was added under N<sub>2</sub> flow, followed, if necessary, by the required amount of solvent. After thermostating at the required temperature for a few minutes, the aldehyde/ketone in the appropriate amount was injected through the septum and time was started.

All reactions were monitored with GC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Separation of the products was performed on 25 m capillary columns using a flame ionization detector. Prior quenching of the catalyst using an excess of LiCl showed no differences in randomly selected analyses.

## 3. Results and discussion

### 3.1. Acetalization of aldehydes and ketones

The first aspect considered was the search for the best operating conditions in the catalytic reaction. To this purpose, complex **1d** was selected as the catalyst for the acetalization of acetaldehyde with EtOH (used both as reactant and as solvent) at  $25^\circ\text{C}$ , taken as a test reaction. The complex was found very active and the results of the effect of a different catalyst to substrate ratio is shown in Fig. 1. The reaction conditions indicated in Fig. 1 and a 1:1000 catalyst to substrate ratio were chosen as the standard for all the reactions reported hereafter. This ratio is a good compromise between the

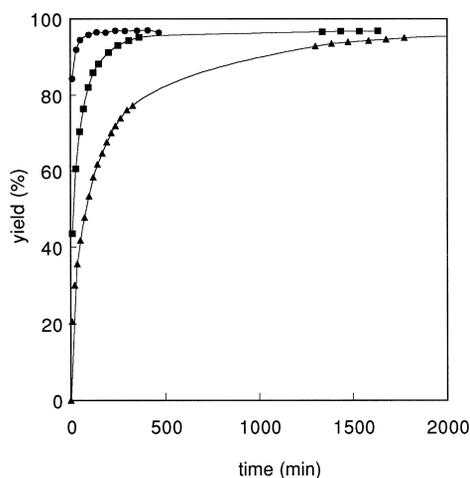


Fig. 1. Effect of different catalyst/substrate ratios in the acetalization of acetaldehyde with ethanol catalyzed by **1d**. Reaction conditions:  $T$   $25^\circ\text{C}$ ; acetaldehyde 10 mmol; EtOH 100 mmol; **1d** 55.6  $\mu\text{mol}$  (circles), 10  $\mu\text{mol}$  (squares), 5  $\mu\text{mol}$  (triangles).

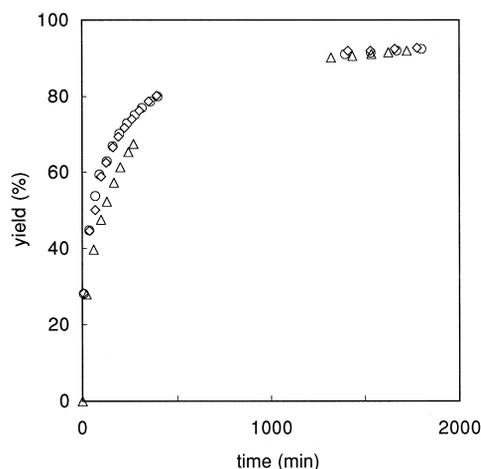


Fig. 2. Effect of the diphosphine in the acetalization of propanal with ethanol catalyzed by **1**. Reaction conditions:  $T$  25°C; propanal 10 mmol; EtOH 100 mmol; **1** 10  $\mu$ mol; catalyst: **1b** (circles), **1c** (diamonds), **1d** (triangles).

observation of a high rate and a good catalyst productivity in terms of turnover number. Where a solvent was used, an amount of alcohol/glycol in the stoichiometric ratio with respect to the aldehyde/ketone was employed.

The effect of the diphosphine on the catalytic activity was tested both in the case of Pd and in the case of Pt complexes. At variance with what has been recently observed in the Baeyer–Villiger oxidation of ketones with the same class of catalysts [21], in the present case the activity is practically unaffected (see for example the case of Pd complexes reported in Fig. 2) by the size of the metal-diphosphine ring, a factor that has been related to the ease with which the hydroxy bridge opens up to produce monomeric, coordinatively unsaturated metal species [21].

A summary of the reactivity of these complexes as catalysts in the acetalization of aldehydes is reported in Table 1. The reaction profiles are in all cases similar to those shown in Figs. 1 and 2,

Table 1

Acetalization of different aldehydes at 25°C catalyzed by hydroxy complexes of palladium and platinum<sup>a</sup>

| Entry | Aldehyde                  | Alcohol        | Catalyst  | Acetal yield (%) |      |
|-------|---------------------------|----------------|-----------|------------------|------|
|       |                           |                |           | 3 h              | 24 h |
| 1     | acetaldehyde              | EtOH           | <b>1d</b> | 75               | 97   |
| 2     | propanal                  | EtOH           | <b>1d</b> | 60               | 91   |
| 3     | propanal                  | EtOH           | <b>2d</b> | 25               | 62   |
| 4     | propanal                  | eth glycol     | <b>1b</b> | 89               | 97   |
| 5     | propanal <sup>b</sup>     | eth glycol     | <b>1b</b> | 33               | 74   |
| 6     | propanal <sup>b</sup>     | eth glycol     | <b>2d</b> | 15               | 55   |
| 7     | propanal <sup>b,c</sup>   | eth glycol     | <b>2d</b> | 76               | 96   |
| 8     | propanal <sup>d</sup>     | eth glycol     | <b>2d</b> | 4                | 21   |
| 9     | propanal                  | 1,3-propandiol | <b>1b</b> | 86               | 98   |
| 10    | octanal                   | EtOH           | <b>1d</b> | 33               | 72   |
| 11    | benzaldehyde              | EtOH           | <b>1d</b> | 47               | 50   |
| 12    | benzaldehyde              | EtOH           | <b>2d</b> | 30               | 40   |
| 13    | <i>m</i> -anisaldehyde    | EtOH           | <b>1d</b> | 18               | 24   |
| 14    | <i>p</i> -Cl-benzaldehyde | EtOH           | <b>1d</b> | 32               | 66   |

<sup>a</sup>Experimental conditions: catalyst 10  $\mu$ mol, aldehyde 10 mmol, alcohol 100 mmol,  $T$  25°C,  $T$  25°C. <sup>b</sup>Glycol 10 mmol, 5.0 ml DCE as solvent. <sup>c</sup> $T$  80°C. <sup>d</sup>5 ml THF as solvent,  $T$  65°C.

hence the yields after 3 h and 24 h are reported in Table 1 as representative of the reactivity in the individual reactions. The selectivity observed was in all cases > 99%, since acetals were the only detectable reaction products.

As can be seen in Table 1 (compare for example entries 5 and 6 or 11 and 12), Pd complexes are in general more reactive than Pt complexes in reactions performed at room temperature, while, on the contrary, they are far less stable for reactions performed at relatively higher temperature (83°C). For example, the reactivity observed in entry 6 with complex **2d** as catalyst at 25°C can be significantly increased (entry 7) by heating at 83°C. The use of **1b** under the same conditions results in the rapid decomposition of the catalyst with loss of any catalytic activity. A solvent effect is evident by comparison of entry 7 and entry 8. The use of a more polar, coordinating solvent such as THF (entry 8) results in a much slower reaction compared to DCE (entry 7) under similar conditions.

With aromatic aldehydes, the reactivity seems to be influenced by the presence of substituents on the aromatic ring capable to alter the electrophilicity of the carbonyl carbon. For example, benzaldehyde (entry 11) reacts more efficiently than *m*-anisaldehyde (entry 13), while *o*- or *p*-anisaldehyde do not react at all. Conversely, a higher yield is observed (entry 14) in the case of *p*-chlorobenzaldehyde.

The acetalization of ketones (Table 2) occurs with features similar to those reported for aldehydes. However, it is generally slower although a better degree of efficiency can be observed by using **2d** at 83°C and/or by increasing the catalyst to substrate ratio (entries 10, 12).

### 3.2. Acetalization with epoxides

The possibility to perform acetalization with epoxides instead of glycols has been recently reported by Zhu and Espenson [16] using methylrhenium trioxide (MTO) as the catalyst. Being the formation of cyclic acetals from glycols an equilibrium reaction, the alternative use of epoxides has the intrinsic advantage of avoiding the formation of water as coproduct, thereby leading, in principle, to more favorable reaction conditions.

The use of epoxides as reactants has been tested with the Pd and Pt catalysts here considered in the case of benzaldehyde and is summarized in Table 3. As can be seen, compared to the use of glycols

Table 2

Acetalization of different ketones at 25°C catalyzed by hydroxy complexes of palladium and platinum<sup>a</sup>

| Entry | Ketone                 | Alcohol    | Solvent | Temp. (°C) | Catalyst  | Acetal yield (%) |      |
|-------|------------------------|------------|---------|------------|-----------|------------------|------|
|       |                        |            |         |            |           | 3 h              | 24 h |
| 1     | cyclohex               | EtOH       | =       | 25         | <b>1d</b> | 2                | 3    |
| 2     | cyclohex               | EtOH       | =       | 25         | <b>2d</b> | 16               | 30   |
| 3     | cyclohex               | eth glycol | =       | 25         | <b>1b</b> | 65               | 96   |
| 4     | cyclohex               | eth glycol | =       | 25         | <b>2d</b> | 45               | 97   |
| 5     | cyclohex               | eth glycol | DCE     | 25         | <b>2d</b> | 5                | 26   |
| 6     | cyclohex               | eth glycol | DCE     | 83         | <b>2d</b> | 75               | 79   |
| 7     | 2-hex                  | eth glycol | =       | 25         | <b>1b</b> | 10               | 58   |
| 8     | 2-hex                  | eth glycol | DCE     | 83         | <b>2d</b> | 50               | 51   |
| 9     | acetoph                | eth glycol | DCE     | 83         | <b>2d</b> | 18               | 24   |
| 10    | acetoph <sup>b</sup>   | eth glycol | DCE     | 83         | <b>2d</b> | 24               | 33   |
| 11    | cyclopent              | eth glycol | DCE     | 83         | <b>2d</b> | 40               | 43   |
| 12    | cyclopent <sup>b</sup> | eth glycol | DCE     | 83         | <b>2d</b> | 52               | 54   |

<sup>a</sup>Experimental conditions: catalyst 10 μmol, ketone 10 mmol, alcohol 100 mmol, T 25°C; in DCE (5 ml) as solvent, alcohol 10 mmol.

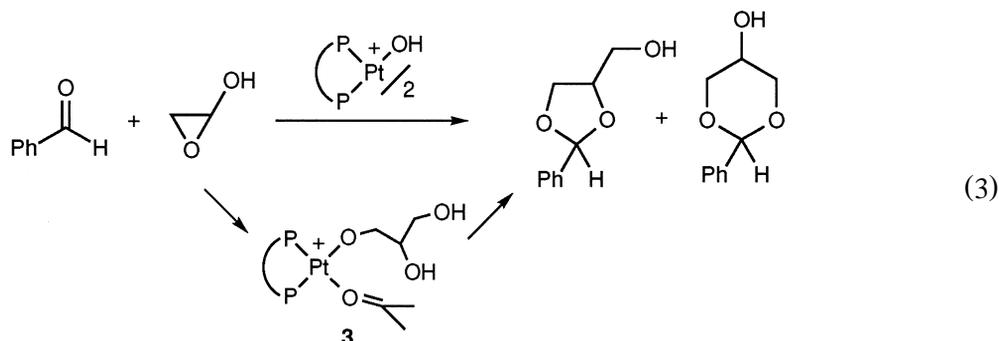
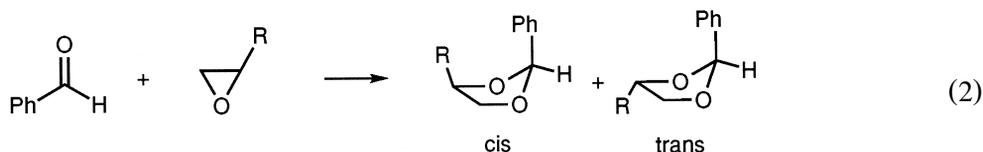
<sup>b</sup>Catalyst 50 μmol.

Table 3  
Acetalization of benzaldehyde with epoxides in DCE catalyzed by Pd and Pt complexes<sup>a</sup>

| Catalyst  | Epoxide                    | Temp. (°C) | Acetal yield (%)                    | <i>cis/trans</i> |
|-----------|----------------------------|------------|-------------------------------------|------------------|
|           |                            |            | 24 h                                |                  |
| <b>1b</b> | propene oxide              | 25         | 16                                  | 1.1              |
| <b>1b</b> | glycidol                   | 25         | 1.4 <sup>b</sup> + 1.7 <sup>c</sup> |                  |
| <b>2d</b> | propene oxide              | 83         | 21                                  | 1.1              |
| <b>1b</b> | propene oxide <sup>d</sup> | 25         | 8                                   | 1.1              |

<sup>a</sup>Experimental conditions: catalyst 10 μmol, benzaldehyde 1 mmol, epoxide 1 mmol, DCE 3 ml, *T* 25°C. <sup>b</sup>Dioxane product. <sup>c</sup>Dioxolane product. <sup>d</sup>Benzaldehyde 10 mmol, epoxide 10 mmol, DCE 5 ml.

under similar conditions the reaction is much slower and less productive. In fact, the yields reported in Table 3 after 24 h are also the maximum yields that can be obtained under the conditions used. According to Eq. (2), the reaction produces two different stereoisomers. The *cis/trans* ratio reported in Table 3 indicates that the stereoselectivity of the system is modest. Furthermore, when using glycidol, the substituted 1,3-dioxane and 1,3-dioxolane are formed (Eq. (3)), albeit in low yields. The formation of two regioisomers from glycidol requires the existence of a common intermediate (probably **3**) which allows the alternative 1,2- or 1,3-addition (Eq. (3)). Compared to MTO the present system is less productive in the acetalization of benzaldehyde, probably reflecting a higher difficulty of the bridging hydroxy complexes to interact with epoxides with respect to MTO. In fact, the latter is known to interact readily with epoxides to yield bis(alcoxy)rhenium (VII) complexes in excellent yields [24] and these intermediates were the access key to the synthesis of acetals [16]. The formation of **3** from **2** requires the protonation of the epoxidic oxygen from the bridging hydroxy ligand, i.e., the existence of an acid character that has been evidenced only in reactions with strong bases such as Li amides [22,25,26]. On the contrary, most of the reactivity of complexes **2** is associated with their basic behavior, as is known from their reactivity and as will be clear from the higher catalytic activity observed for 1,2-propanediol and glycerol reported in Section 3.3.



### 3.3. Stereoselective reactions

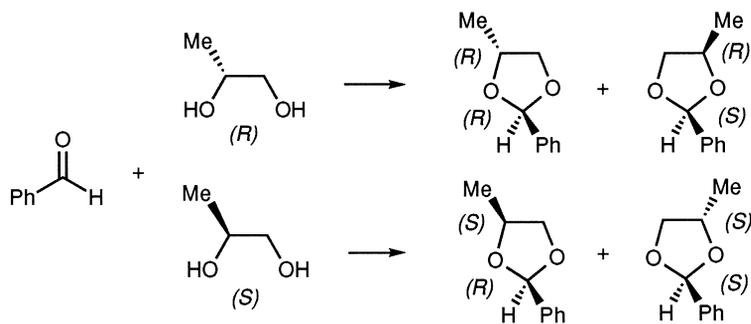
The reaction between most carbonyl compounds and epoxides or glycols such as propene oxide, 1,2-propanediol, glycidol, or glycerol entails some stereochemical aspects that were considered worthwhile of investigation. In fact, depending on the orientation with which the glycol (epoxide) binds the carbonyl compound different stereoisomers can be formed. Hereafter, only the case of glycols will be considered, because, being more reactive, they allow an easier characterization of the stereoisomers formed in the reaction. The same considerations apply also to epoxides. The case of benzaldehyde and 1,2-propanediol is shown as an example in Scheme 1. The situation is complicated by the fact that 1,2-propanediol is a chiral molecule, so that four different stereoisomers (two couples of enantiomers) may form. The process consists of two parallel diastereoselective reactions in which either 1,2-propanediol enantiomer induces the formation of a new stereocenter leading to the formation of diastereoisomers.

The use of racemic 1,2-propanediol led to the formation of all four predicted stereoisomers (Scheme 1). Analysis of the reaction mixture was performed by GC using a chiral column. Unfortunately, the separation of the enantiomers was largely incomplete, preventing an assessment of the stereochemistry of the reaction.

The study of the system was simplified by using (*R*)-1,2-propanediol as the reactant. All reactions were performed at 25°C and the results are summarized in Table 4. GC analysis on the chiral column allowed the separation of the diastereoisomers and the calculation of the diastereomeric excess (d.e.). As can be seen (compare entries 1 and 2 of Table 4), the use of DCE as solvent improves the d.e. significantly, while only modest differences are observed on going from Pd to Pt complexes. We thought also of interest to see whether the use of a chiral catalyst had an influence on the diastereoselectivity of the reaction and to this purpose the binap derivatives of Pd (**1e**) and Pt (**2e**) were tested. As is clear from entries 3 and 5, no difference is observed, suggesting that the stereochemistry of the reaction is controlled mainly by the stereocenter in the glycol reactant.

Finally, the reaction between benzaldehyde and glycerol was studied. Although glycerol is an achiral molecule the same mixture of stereoisomers shown in Scheme 1 is obtained, because two stereocenters originate during the course of the reaction. However, glycerol entails also a problem of regioselectivity (see above the case of glycidol), since 1–2 and 1–3 addition products (dioxolanes and dioxanes, respectively) can be formed, the latter existing either in *cis* or *trans* configuration (Scheme 2).

The catalysts tested were **1b**, **1e**, **2d**, and **2e**. In these experiments, GC analysis of the reaction mixtures with the chiral column allowed the separation of all six isomers. Best results are obtained in



Scheme 1.

Table 4

Catalytic acetalization of benzaldehyde with *R*-propene glycol: yields and diastereomeric excess of the product<sup>a</sup>

| Entry | Catalyst               | Acetal yield (%) |      | d.e. (%) |
|-------|------------------------|------------------|------|----------|
|       |                        | 3 h              | 24 h |          |
| 1     | <b>1b</b> <sup>b</sup> | 87               | 91   | 32       |
| 2     | <b>1b</b>              | 41               | 62   | 60       |
| 3     | <b>1e</b>              | 23               | 45   | 60       |
| 4     | <b>2d</b>              | 26               | 50   | 51       |
| 5     | <b>2e</b>              | 33               | 54   | 50       |

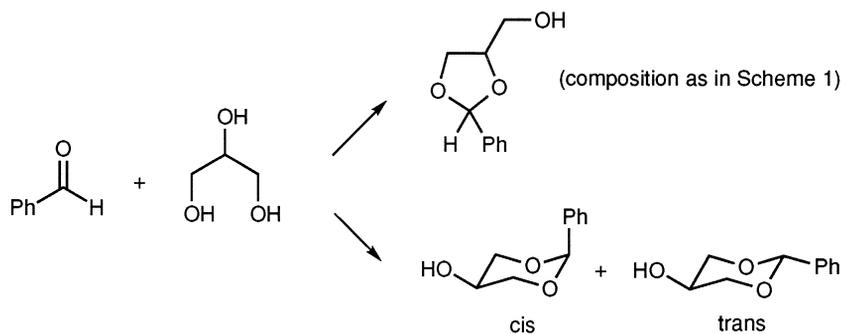
<sup>a</sup>Reaction conditions: catalyst 10  $\mu$ mol, benzaldehyde 10 mmol, glycol 10 mmol, DCE 6.6 ml, *T* 25°C. <sup>b</sup>No solvent, glycol 100 mmol.

the absence of solvent (yields in the range of 90%) and the formation of 1,3-dioxolanes is generally favored with respect to 1,3-dioxanes. However, a reaction profile (Fig. 3) indicates that for longer reaction times, when the acetalization reaction is finished and the conversion is constant, part of the 1,3-dioxolanes tend to be converted into 1,3-dioxanes. This seems to suggest the occurrence of a consecutive reaction in which the kinetically favored dioxolanes are slowly reconverted into the thermodynamically more stable dioxanes. Other features of these reactions are the following: (i) the *trans/cis* 1,3-dioxanes ratio is always close to 2 and in favor of the more thermodynamically stable *trans* isomer, (ii) the four 1,3-dioxanes are present in virtually identical amounts ( $\sim 25\%$  each). These results are observed with all catalysts including the chiral Pd and Pt complexes, which again seem to have no control on the isomeric composition of the 1,3-dioxolanes and 1,3-dioxanes mixtures.

### 3.4. Mechanistic considerations

A possible mechanism for the acetalization of carbonyl compounds using bis(aquo)-Pd(II) and -Pt(II) complexes as catalysts has been suggested by Gorla and Venanzi [18]. This mechanistic suggestion can easily apply to the present system with some minor modifications and is shown in Scheme 3. The only difference with the proposal of Gorla and Venanzi is in the initial steps that lead to the formation of **5**.

The genesis of **4** requires the protonation of the bridging hydroxy ligand by an incoming alcohol molecule. Evidence for the basic character of the bridging  $-\text{OH}$  ligand in  $[(\text{P}-\text{P})\text{Pt}(\mu\text{-OH})]_2^{2+}$  complexes has been found by us [27] and other groups [18,23,28,29] in the reaction with a variety of strong and weak acids leading to condensation products. Experimental evidence for the existence of a species like **4** was found by analyzing the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2d** in  $\text{CD}_3\text{OD}$ . The spectrum



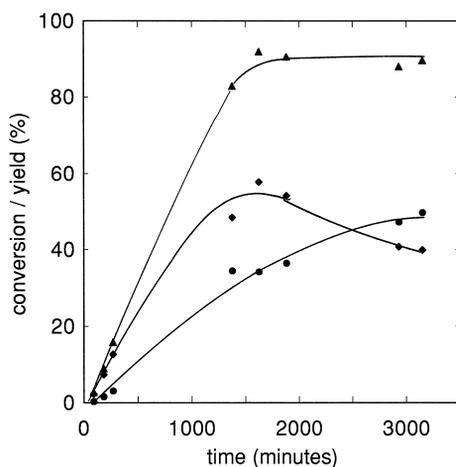
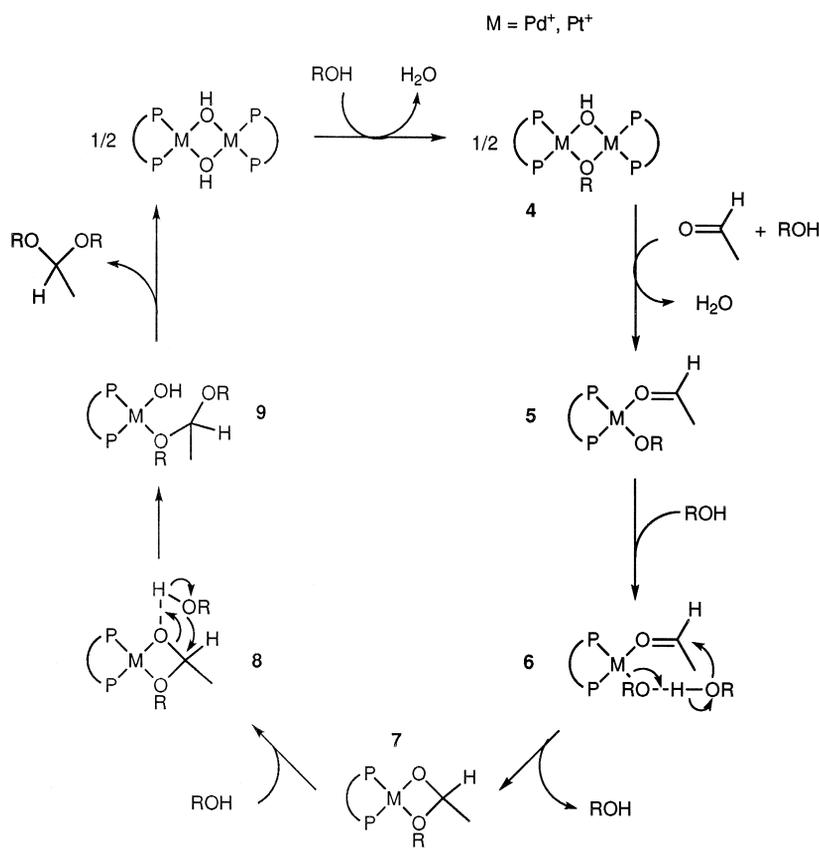


Fig. 3. Acetalization of benzaldehyde with glycerol catalyzed by **1b**. Reaction conditions as in Fig. 2. Conversion (triangles), yield in dioxolane (diamonds), yield in dioxane (circles).

shows the existence of a mixture of two products: **2d** ( $\delta$  5.84 ppm;  $^1J_{P-Pt}$  3514 Hz) [21,22] and a new species ( $\delta$  2.84 ppm;  $^1J_{P-Pt}$  3409 Hz,  $^2J_{P-P}$  24.6 Hz;  $\delta$  5.87 ppm;  $^1J_{P-Pt}$  3574 Hz,  $^2J_{P-P}$  24.6 Hz) in an approximately 1:5 ratio. The existence of two independent P nuclei and the extent of the coupling



constants suggest for the new species a formulation such as in **4**, which is homologous to that found in reactions with carboxylic acids [27]. Addition of an excess of propanal, to mimic the catalytic reaction conditions, reverted the initial equilibrium (water is produced by the catalytic reaction) with **2d** as the major product, leaving only minor amounts of the species similar to **4**, and showing the formation of a weak unresolved multiplet around 4 ppm, probably a mixture of different reaction intermediates.

The formation of **5** by displacement of water results in the increase of the electrophilic character of the aldehyde/ketone making it more reactive towards the nucleophilic attack by the alcohol. Species homologous to **5**, such as  $[(\text{dppb})\text{Pt}(\text{ketone})(\text{OOH})]^+$ , have been evidenced as the key intermediate in a mechanistic study of the Baeyer–Villiger oxidation of ketones with hydrogen peroxide catalyzed by **2d** [21]. The transformation of **5** into **7** and **7** into **9** are suggested to occur via the formation of cyclic structures (**6** and **8**) in which hydrogen bonding forms between the free alcohol and the coordinated alcoxide. Structures of this type have been already described in the case of Pd [30]. On the other hand, the coordination chemistry of Pt complexes with bidentate O-donor ligands, forming 4-membered rings, such as  $\text{CO}_3^{2-}$ ,  $\text{RCO}_2^-$  is well established [31,32], and thus, the direct transformation of **5** into **7** by a direct intramolecular reaction cannot, in principle, be excluded.

The reaction sequence from **5** to **9**, which is speculative and identical to the proposal of Gorla and Venanzi [18], may seem exceedingly complex. However, the process going from **5** to **7** is responsible for the genesis of the chiral center in the reactant when certain glycols are used (see above). Since the degree of control of the (chiral) catalyst in asymmetric transformations is practically negligible, this finding can be more easily explained by an external attack of the alcohol such as in **6** or **8** and is an indirect but important piece of support to the suggestions of Gorla and Venanzi. Under this hypothesis, the metal behaves mainly as a Lewis acid increasing the electrophilicity of the carbonyl carbon by coordination, while, at the same time, improving the reactivity of the alcohol via hydrogen bonding with the coordinated alcoxide.

#### 4. Conclusions

The results here reported represent one of the few examples of transition metal catalysis applied to the acetalization of aldehydes and ketones with alcohols or glycols. Ambiguities arising from  $\text{H}^+$  generated in the system seem to be excluded by the chemistry known for this class of bridging hydroxo complexes of palladium and platinum which behave as bases capable of reacting with (weak) acids with formation of water. Apart from this intrinsic advantage, the main features of the acetalization reaction are rather disappointing. The lack of any effect on the reactivity induced by the steric properties of different diphosphines and the lack of stereochemical control by the catalyst in stereoselective reactions, seem to suggest for the cationic metal centers a role very close to that of a simple Lewis acid. The notable reactivity of the catalysts and the possibility to use platinum complexes at moderately high temperatures recommend for the system the use towards aldehydes or ketones which cannot be acetalized under acid catalysis, that are currently being tested.

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