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Palladium^0-catalyzed isomerization of (*Z*)-1-functionalized-4-acetoxy-2-butenes: Solvent and substituent effects

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ABSTRACT

The $Pd(PPh_3)_4$-catalyzed isomerization of (*Z*)-1,4-diacetoxy-2-butene, (*Z*)-1-(*t*-butyldimethylsilyloxy)-4-acetoxy-2-butene and (*Z*)-1-(*t*-butyldiphenylsilyloxy)-4-acetoxy-2-butene affords the corresponding (*E*)-isomers and 1,2-difunctionalized-3-butenes. In THF, the formation of the (*E*)-isomers is mainly due to reaction from an η^1-allylpalladium intermediate while an η^3-allylpalladium is the main key intermediate in DMF. The time to reach equilibrium between the products and their respective concentrations depend on the nature of the substituents and the solvent.

1. Introduction

The 1,3-transposition of allylic acetates in the presence of catalytic amounts of palladium complexes is a well known reaction [1], which has been extensively used in synthetic organic chemistry. We have previously reported the isomerisation of (*Z*)-1,4-diacetoxy-2-butene (**1**$_{Ac}$) using catalytic amounts of $Pd(PPh_3)_4$ or $PdCl_2(MeCN)_2$ in THF and DMF [2,3]. With the Pd^0 catalyst, we have demonstrated that **1**$_{Ac}$ was selectively isomerized to (*E*)-1,4-diacetoxy-2-butene (**2**$_{Ac}$) in THF while both **2**$_{Ac}$ and 1,2-diacetoxy-3-butene (**3**$_{Ac}$) were simultaneously obtained in DMF (Scheme 1) [2].[1] A set of experiments, examined in the light of Amatore and Jutand et al. results [4], has led to conclude to the involvement of an η^1-allylpalladium complex in the former solvent, and of an η^3-allylpalladium complex in the latter as the key intermediates from **1**$_{Ac}$. We have envisaged that the unexpected behavior of **1**$_{Ac}$ in THF could be due to the intramolecular stabilization of the η^1-allylpalladium intermediate by ligation of the acetate unit, giving rise to the complex **C′**$_{Ac}$ possessing a 16-electron configuration as depicted in Scheme 2. This hypothesis urges us to investigate the Pd^0-catalyzed isomerization of (*Z*)-1-(*t*-butyldimethylsilyloxy)-4-acetoxy-2-butene (**1**$_{Sm}$) and (*Z*)-1-(*t*-butyldiphenylsilyloxy)-4-acetoxy-2-butene (**1**$_{Sp}$) under the same conditions. Given the obtained results, we have also monitored the corresponding reactivity of (*E*)-1-(*t*-butyldimethylsilyloxy)-4-acetoxy-2-butene (**2**$_{Sm}$) and 1-(*t*-butyldimethylsilyloxy)-2-acetoxy-3-butene (**3**$_{Sm}$). Here is reported this study.

2. Results

The reaction of **1**$_{Sm}$ induced by 0.05 equiv. of $Pd(PPh_3)_4$ in refluxing THF afforded (*E*)-1-(*t*-butyldimethylsilyloxy)-4-acetoxy-2-butene (**2**$_{Sm}$) and 1-(*t*-butyldimethylsilyloxy)-2-acetoxy-3-butene (**3**$_{Sm}$) (Eq. (1)). Monitoring the isomerization by GC (Fig. 1 and Table S1)[2] showed that the quantity of **2**$_{Sm}$ reached a maximum after 15–20 min and then decreased, leading to an equilibrium between the three isomers after 50–60 min with an **1**$_{Sm}$/**2**$_{Sm}$/**3**$_{Sm}$ ratio, noted **E**$_{Sm,THF}$, estimated to ca. 4:60:36.

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[1] For our previous reported studies, the Pd^0-catalyzed isomerization of **1**$_{Ac}$ was monitored using ^1H NMR [2]. In repeating the monitoring of this reaction using HPLC, we have observed that this isomerization led to an equilibrium between **1**$_{Ac}$, **2**$_{Ac}$ and **3**$_{Ac}$, the quantity of **1**$_{Ac}$ being 2–3%.

[2] Given the accuracy of the GC and HPLC analysis, the values of the proportions of the isomers indicated in Tables S1–S6 are at ±1.

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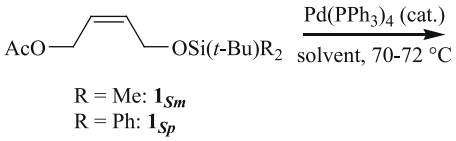

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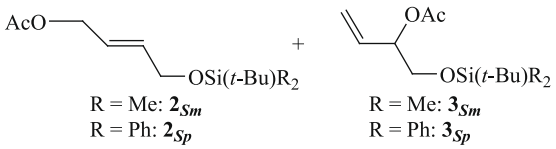
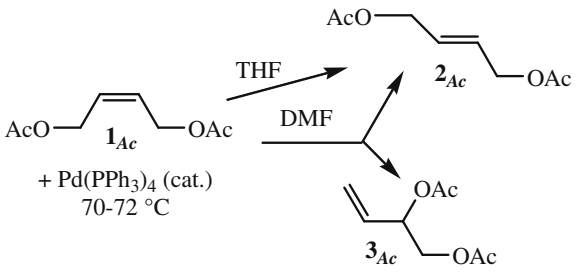




Scheme 1.

Switching from THF to DMF as solvent led at 70 °C to a fast reaction: the proportions of $\mathbf{1}_{Sm}$, $\mathbf{2}_{Sm}$ and $\mathbf{3}_{Sm}$ did not evolve after 1 min (Fig. 2 and *Table* S2), the $\mathbf{1}_{Sm}/\mathbf{2}_{Sm}/\mathbf{3}_{Sm}$ noted $\mathbf{E}_{Sm,DMF}$ being ca. 4:70:26.

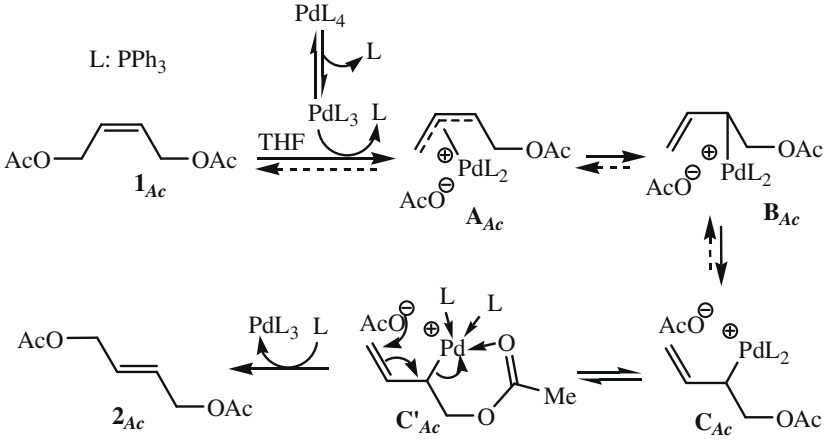
In THF, the amount of the (*E*)-isomer from $\mathbf{1}_{Sp}$ reached a maximum after 25–35 min and the $\mathbf{1}_{Sp}/\mathbf{2}_{Sp}/\mathbf{3}_{Sp}$ equilibrium ($\mathbf{E}_{Sp,THF} \approx 2{:}66{:}32$) was attained after ca. 80 min (Fig. 3 and *Table* S3). In DMF, the equilibrium ($\mathbf{E}_{Sp,DMF} \approx 6{:}69{:}25$) was attained after ca. 7 min (Fig. 4 and *Table* S4).

The isomerization of $\mathbf{2}_{Sm}$ and $\mathbf{3}_{Sm}$ has been examined only in THF (*Tables* S5 and S6). The $\mathbf{2}_{Sm} \rightarrow \mathbf{1}_{Sm} + \mathbf{3}_{Sm}$ and $\mathbf{3}_{Sm} \rightarrow \mathbf{1}_{Sm} + \mathbf{2}_{Sm}$ were observed with equilibria between the three compounds attained after 90–220 min.

To resume the previous [2][1] and present results, the reaction times to attain the equilibrium, noted $\mathbf{TE}_{Y,solvent}$, and the corresponding relative amounts of the three isomers (noted $\mathbf{E}_{Y,solvent}$) from $\mathbf{1}_{Ac}$, $\mathbf{1}_{Sp}$, $\mathbf{1}_{Sm}$, $\mathbf{2}_{Sm}$ and $\mathbf{3}_{Sm}$, are listed in Table 1.

3. Discussion

From the results assembled in Figs. 1 and 3 and those previously obtained from $\mathbf{1}_{Ac}$ [2], it appears that the concentration, in THF, of the (*E*)-isomer versus time from $\mathbf{1}_{Ac}$, $\mathbf{1}_{Sm}$ and $\mathbf{1}_{Sp}$ went trough a maximum before to decrease. Consequently, we assume that the



Scheme 2.

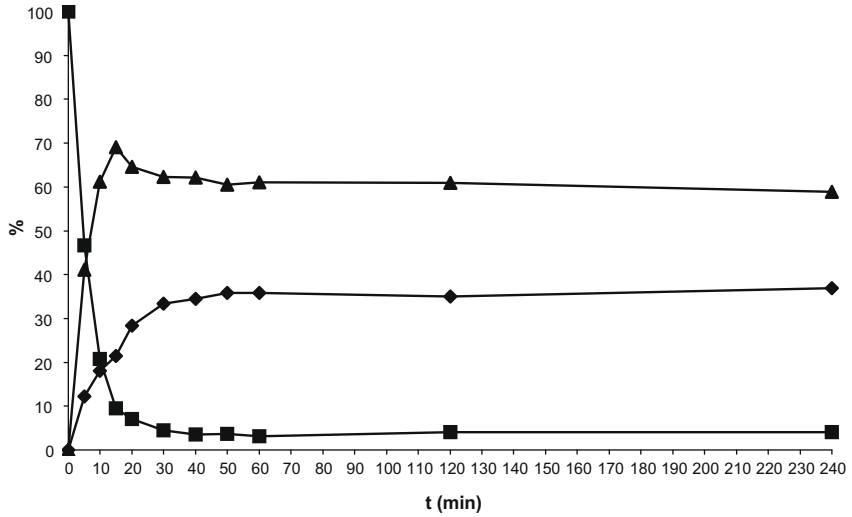


Fig. 1. Evolution over time of the proportions of $\mathbf{1}_{Sm}$ (■), $\mathbf{2}_{Sm}$ (▲) and $\mathbf{3}_{Sm}$ (♦) from the $Pd(PPh_3)_4$-catalyzed reaction of $\mathbf{1}_{Sm}$ in refluxing THF.

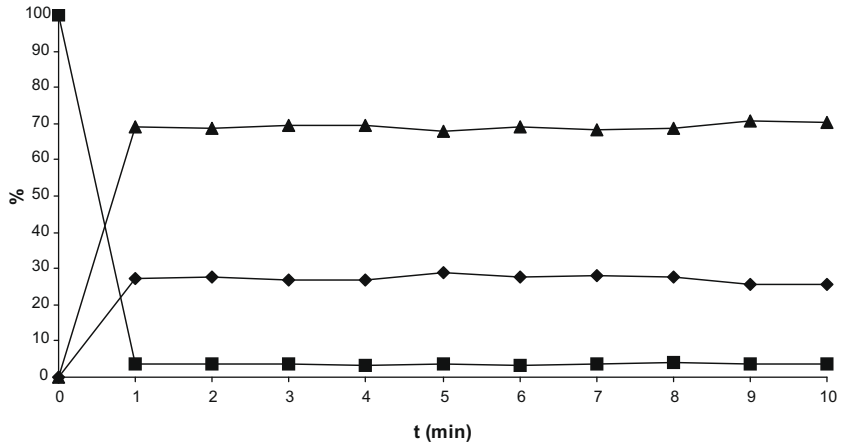


Fig. 2. Evolution over time of the proportions of $\mathbf{1}_{Sm}$ (■), $\mathbf{2}_{Sm}$ (▲) and $\mathbf{3}_{Sm}$ (♦) from the $Pd(PPh_3)_4$-catalyzed reaction of $\mathbf{1}_{Sm}$ in DMF at 70 °C.

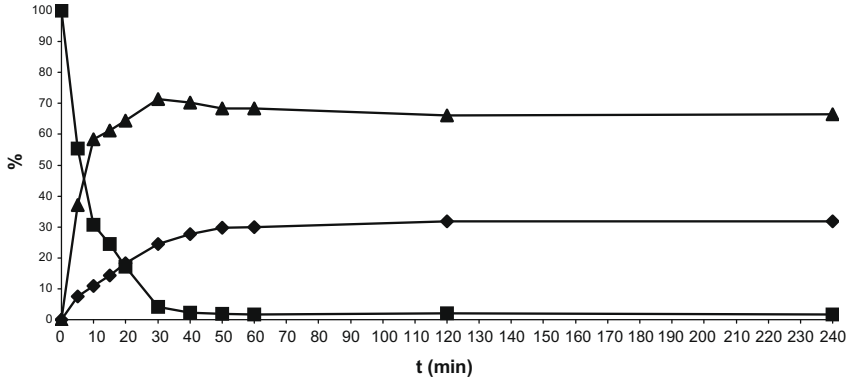


Fig. 3. Evolution over time of the proportions of $\mathbf{1}_{Sp}$ (■), $\mathbf{2}_{Sp}$ (▲) and $\mathbf{3}_{Sp}$ (♦) from the $Pd(PPh_3)_4$-catalyzed reaction of $\mathbf{1}_{Sp}$ in refluxing THF.

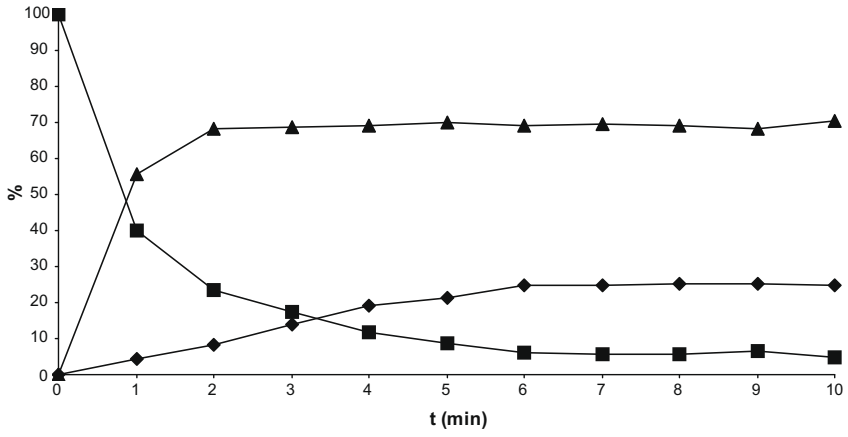
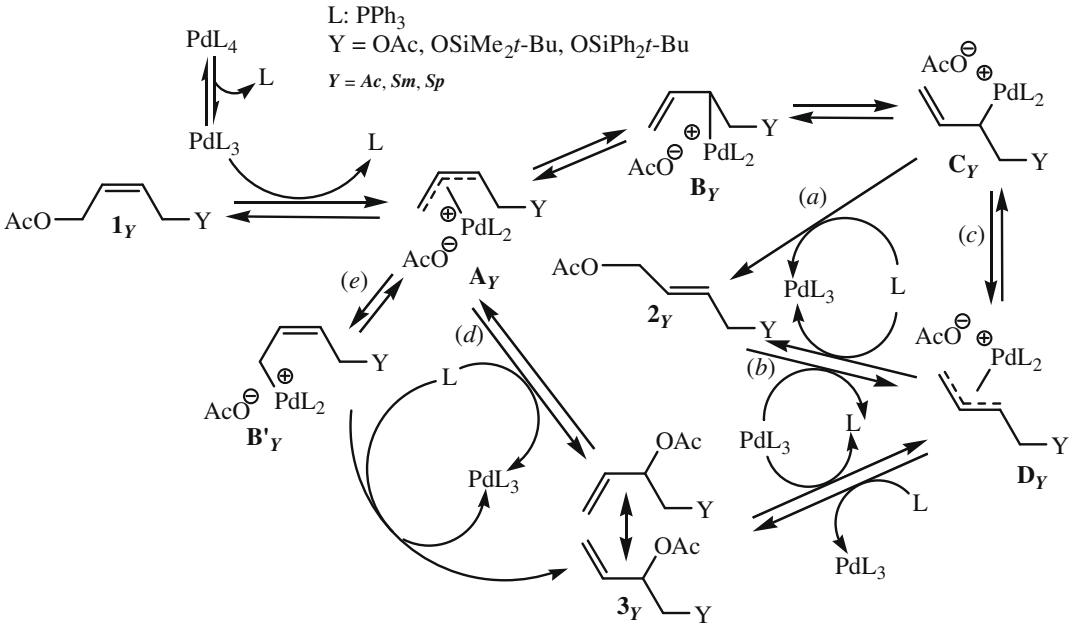


Fig. 4. Evolution over time of the proportions of $\mathbf{1}_{Sp}$ (■), $\mathbf{2}_{Sp}$ (▲) and $\mathbf{3}_{Sp}$ (♦) from the $Pd(PPh_3)_4$-catalyzed reaction of $\mathbf{1}_{Sp}$ in DMF at 70 °C.

Table 1
Influence of the nature of Y and the solvent on the equilibria.

		Substrate				
	Solvent	$\mathbf{1}_{Ac}$	$\mathbf{1}_{Sp}$	$\mathbf{1}_{Sm}$	$\mathbf{2}_{Sm}$	$\mathbf{3}_{Sm}$
Reaction time for the equilibrium = $\mathbf{TE}_{Y,solvent}$	THF	≈45 min	≈80 min	≈55 min	≈100 min	≈200 min
	DMF	≈30 min	≈7 min	≈1 min		
$\mathbf{1}_Y$:$\mathbf{2}_Y$:$\mathbf{3}_Y$ at equilibrium = $\mathbf{E}_{Y,solvent}$	THF	≈2:60:38	≈2:66:32	≈4:60:36	≈4:59:37	≈4:59:37
	DMF	≈2:62:36	≈6:69:25	≈4:70:26		



Scheme 3.

formation of $\mathbf{2}_{Ac}$ from an η^1-allylpalladium rather than from an η^3-allylpalladium is not due to the possible stabilization of the former complex by coordination of the OAc unit leading to $\mathbf{C'}_{Ac}$ (Scheme 2). As from $\mathbf{1}_{Ac}$, the shape, in DMF, of the curves corresponding to the concentration of (*E*)-isomers $\mathbf{2}_{Sm}$ and $\mathbf{2}_{Sp}$ did not indicate the presence of a maximum before the equilibrium (Figs. 2 and 4). Given these observations, a mechanistic scheme common to $\mathbf{1}_{Ac}$, $\mathbf{1}_{Sm}$ and $\mathbf{1}_{Sp}$ can be proposed in taking into account the following Amatore and Jutand remark: "ions pairs $[(\eta^3\text{-}CH_2CHCH_2)Pd(PPh_3)_2{}^+AcO^-]$ are formed in THF whereas free ions are formed in DMF" [4,5].

In THF, the main reactive pathway at the beginning of the transformation of $\mathbf{1}_Y$ is the formation of $\mathbf{2}_Y$ via tight ion pairs $\mathbf{A}_Y$, $\mathbf{B}_Y$ and $\mathbf{C}_Y$ as intermediates (Scheme 3, path *a*). According to previous results [2] and those from $\mathbf{1}_{Sm}$, $\mathbf{1}_Y$ evolves more rapidly than $\mathbf{2}_Y$. Consequently, a relative high conversion of $\mathbf{1}_Y$ is attained before one observes 1,3-transposition of $\mathbf{2}_Y$ into $\mathbf{3}_Y$ (path *b*). Concurrent reactive pathways leading to $\mathbf{3}_Y$ could involve the $\mathbf{C}_Y \rightarrow \mathbf{D}_Y$ transformation (path *c*) and reaction from $\mathbf{A}_Y$ with possibly $\mathbf{B'}_Y$ as intermediate (paths *d* and *e*).

We have previously shown that, in DMF, $\mathbf{2}_{Ac}$ and $\mathbf{3}_{Ac}$ are concomitantly produced from $\mathbf{1}_{Ac}$, the $\mathbf{2}_{Ac}/\mathbf{3}_{Ac}$ ratio being ca. 1.7 throughout the entire reaction [2]. While equilibrium from $\mathbf{1}_{Sm}$ is obtained too rapidly (Fig. 2) to make valuable comments on the formation of $\mathbf{2}_{Sm}$ and $\mathbf{3}_{Sm}$, the reaction from $\mathbf{1}_{Sp}$ is, according to Fig. 4, rather similar to that from $\mathbf{1}_{Ac}$. Nevertheless, the $\mathbf{2}_{Sp}/\mathbf{3}_{Sp}$ ratio decreased with time from ca. 13 after 1 min of reaction, to 2.8 at the equilibrium (Table S4).[3] The separation of the ions in DMF [4,5] led the $\mathbf{C}_Y \rightarrow \mathbf{D}_Y$ transformation (path *c*) to effectively compete with the $\mathbf{C}_Y \rightarrow \mathbf{2}_Y$ step (path *a*). Consequently, $\mathbf{2}_Y$ and $\mathbf{3}_Y$ can be both produced from $\mathbf{D}_Y$. The non-linearity with time of the $\mathbf{2}_{Sp}/\mathbf{3}_{Sp}$ ratio led us, however, to suspect that some $\mathbf{2}_{Sp}$ is produced via path *a* even in DMF. Since the $\mathbf{2}_{Sp}/\mathbf{3}_{Sp}$ ratio is always widely >1, the formation of $\mathbf{3}_{Sp}$ from $\mathbf{A}_Y$ via path *d* or *e* is, at the best, a very limited reactive process.

As shown in Table 1, the $\mathbf{TE}_{Y,solvent}$ depends on Y, in particular when DMF is the solvent. Indeed, the reaction time in DMF for the equilibrium varies from a few min when Y = $SiMe_2t$-Bu or $SiPh_2t$-Bu to 30 min when Y = OAc. The differences are much lower in THF, in which the main reactive pathway is $\mathbf{1}_Y \rightarrow \mathbf{A}_Y \rightarrow \mathbf{B}_Y \rightarrow \mathbf{C}_Y \rightarrow \mathbf{2}_Y$. A possible explanation of the greatest $\mathbf{TE}_{Ac,DMF}$ could be the already suspected stabilization of $\mathbf{C}_{Ac}$ by the acetate unit leading to $\mathbf{C'}_{Ac}$ (Scheme 2). The absence of such stabilization when $\mathbf{1}_{Sm}$ and $\mathbf{1}_{Sp}$ are the substrates, would facilitate the transformation of the η^1-allylpalladium into the η^3-allylpalladium, i.e. the $\mathbf{C}_{Sm} \rightarrow \mathbf{D}_{Sm}$ and $\mathbf{C}_{Sp} \rightarrow \mathbf{D}_{Sp}$ pathways, hence a faster equilibrium.

The dependence of the $\mathbf{2}_Y/\mathbf{3}_y$ ratios with the nature of Y is particularly observed in DMF (Table 1). This can be explained in considering the $\mathbf{D}_Y \rightarrow \mathbf{2}_Y + \mathbf{3}_Y$ transformation. Due to its polarity [6], DMF solvates efficiency the acetate anion [7] yielding bulky nucleophilic species. Consequently, steric repulsions between these species and Y increase with the size of this latter leading to a decrease of the $\mathbf{D}_Y \rightarrow \mathbf{3}_Y$ reaction at the benefit of the $\mathbf{D}_Y \rightarrow \mathbf{2}_Y$ reaction, hence $\mathbf{2}_{Ac}/\mathbf{3}_{Ac}$ ratio lower than the $\mathbf{2}_{Sp}/\mathbf{3}_{Sp}$ and $\mathbf{2}_{Sm}/\mathbf{3}_{Sm}$ ratios. The acetate anion being less prone to solvation in THF, the OAc/Y interactions are lower and, consequently, the difference in the two reactive pathways occurring from $\mathbf{D}_Y$ is also decreased.

The nature of the solvent may also affect the equilibrium ($\mathbf{E}_{Y,solvent}$) between the three isomers (Table 1). This is highlighted from $\mathbf{1}_{Sp}$ and $\mathbf{1}_{Sm}$, and could be due to the coordinating properties of DMF towards the transition metals [4,5,8,9]. It is known that DMF can substitute coordinated PPh_3 [10], and that the equilibria attained from the Pd^0-catalyzed 1,3-transposition of allylic acetates is ligand dependent [11]. Thus, coordination of DMF to the palladium intermediates depicted in Scheme 3 can have an effect on equilibria and reaction rates.

In conclusion, the mechanism of the Pd^0-catalyzed isomerization of allylic acetates depends on the dissociating, solvating and coordinating properties of the solvent.

Acknowledgement

We are grateful to CNRS for a temporary position to A.M.Z.

[3] The isomerization of $\mathbf{1}_{Sp}$ and corresponding GC monitoring have been carried out twice: similar results have been obtained from one experiment to the other.

Appendix A. Supplementary material

Supplementary data associated with this article (Tables S1–S6. Synthesis of $\mathbf{1}_{Sm}$, $\mathbf{1}_{Sp}$. Isomerization and analysis procedures.) can be found, in the online version, at doi:10.1016/j.jorganchem.2009.09.028.

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