Palladium(0)-Catalyzed Isomerization of (*Z*)-1,4-Diacetoxy-2-butene − Dependence of η^1- or η^3-Allylpalladium as a Key Intermediate on the Solvent Polarity

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Keywords: Allyl ligands / Coordination modes / Isomerization / Palladium / Catalysis / Solvent effects

In the presence of $Pd(PPh_3)_4$, (Z)-1,4-diacetoxy-2-butene is selectively isomerized to (*E*)-1,4-diacetoxy-2-butene in THF while both (*E*)-1,4-diacetoxy-2-butene and 1,2-diacetoxy-3-butene are obtained in DMF. Evidence to support the involvement of an η^1-allylpalladium in the former solvent and of a cationic η^3-allylpalladium in the latter as the keys intermediates is presented.

Introduction

The palladium(0)-catalyzed alkylation of allylic acetates is a reaction extensively used in organic synthesis for which the commonly accepted mechanism involves cationic η^3-allylpalladium intermediates.[1,2] Two decades ago, Fiaud and Malleron suggested that this reaction does not only involve such an intermediate but could also involve a nucleophilic addition to a cationic η^1-allylpalladium intermediate.[3] This proposition was promptly rejected by Trost and Schmuff.[4] However, returning to this subject fifteen years later, Trost and Bunt[5] proposed the formation in a rather nonpolar solvent such as THF of an intimate or tight ion pair between the cationic η^3-allylpalladium intermediate and the acetate anion, and that such an ion pair is nonsymmetrical; they concluded that "the invoking of a nonsymmetrical intimate ion pair nicely accounts for the apparent dichotomy" between the two earlier reports.[3,4] These studies have induced meticulous work around the concept of the memory effect.[6] Recently, Amatore and Jutand et al.[7] have superbly demonstrated the influence of the nature of the solvent on the species formed from allyl acetate, $Pd(dba)_2$ and PPh_3: "in THF, the acetate ion sticks on the palladium(II) complex (ion pair)"[8,9] while "in DMF (free ions), the acetate is located far from the cationic π-allylpalladium(II) center".

Allylic acetates subjected to Pd^0-catalysis in the absence of added nucleophile can suffer *Z*/*E*-isomerization,[10] 1,3-transposition[11] and also epimerization when the substrates are chiral.[6b,12−14] To rationalize the 1,3-transposition, an internal return of the acetate anion either at the level of the cationic η^3-allylpalladium complex[12] or through the concerted rearrangement of a neutral acetoxy-(η^1-allyl)palladium complex[11a] has been proposed; subsequent studies using labeled acetates suggested the former as the key intermediate.[6a,11c] Furthermore, the reversible formation of η^3-allylpalladium complexes from allylic acetates has been observed.[6b,7,12,15]

(*Z*)-1,4-Diacetoxy-2-butene (**1**) has been extensively used as a synthon for the synthesis of various compounds under Pd^0 catalysis.[16] Furthermore, Golding et al. have briefly reported that the treatment of **1** with a catalytic quantity of $Pd(PPh_3)_4$ in benzene at room temperature led to (*E*)-1,4-diacetoxy-2-butene (**2**) in high yield.[10] The authors proposed that this *Z* to *E* isomerization involves an initial 1,3-rearrangement to 1,2-diacetoxy-3-butene (**3**), which was not isolated, followed by a further 1,3-rearrangement to **2**.[10] In considering their previous report,[11c] that means they presumed two successive η^3-allylpalladium intermediates leading to **3** and **2** respectively. A few years ago, we synthesized enantiopure vinylmorpholines by the Pd^0-catalyzed diastereoselective disubstitution of **1** by chiral amino alcohols in refluxing THF.[17] In the course of the study, we became interested in the course of the Pd^0-catalyzed isomerization of **1**.[18] The unexpected results we obtained led us to examine the reactivity of **2** and **3** under similar conditions and then to use a more polar solvent than THF. These studies, presented here, exemplify the determinant role of the interactions between the palladium(II) center and the acetate anion during the isomerization of **1**.

Results and Discussion

In the presence of 0.05 equiv. of $Pd(PPh_3)_4$, **1** is rapidly isomerized in refluxing THF. By monitoring the reaction[19] (Figure 1, Table S1), we observed more than 50% isomerization in 5 min. and the predominant formation of **2**. The quantity of **2** increased initially but, surprisingly, reached a maximum at 15 min. and then decreased. An equilibrium mixture which contained exclusively **2** and **3** (**2**/**3** = 1.78 ± 0.12), was obtained within ca. 45 min. These observations

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  1434−193X/01/0917−3301 $ 17.50+.50/0

indicated that **1** affords mainly or exclusively **2**, while **3** is produced by isomerization of **2**. This differs from the sequence **1**→ **3** → **2** proposed by Golding et al. (vide supra) for the isomerization at room temperature in another nonpolar solvent.[10] The selective isomerization of **2** → **3** under our experimental conditions has been confirmed by using **2** as substrate (Figure 2, Table S2); no trace of **1** was detected and the final ratio of **2/3** was 1.56 ± 0.11. Since the final product distributions obtained from **1** and **2** were of the same order, a Pd^0-catalyzed thermodynamic equilibrium between **2** and **3** is suggested. Indeed, a similar ratio was obtained from **3** within ca. 25 min. (Figure 3, Table S3, **2/3** = 1.71 ± 0.11). Note that no products other than **1**, **2** and **3** were detected by ^1H NMR analysis of the crude reaction mixtures, and almost quantitative yields of diacetates were obtained on workup.

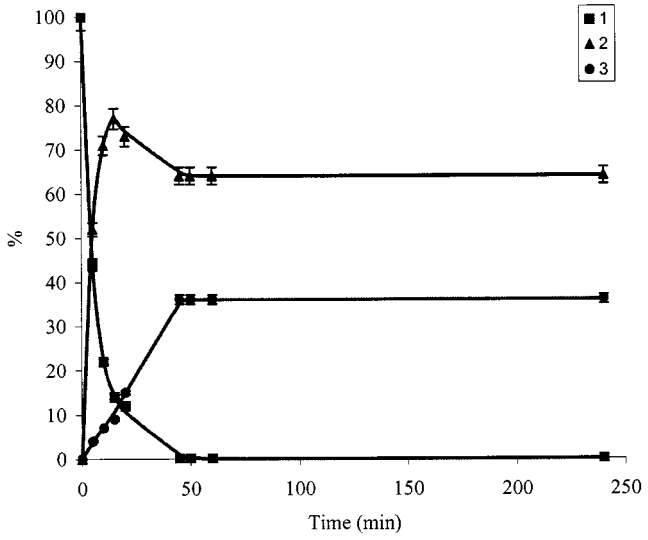


Figure 1. Diacetate proportions from **1** in THF

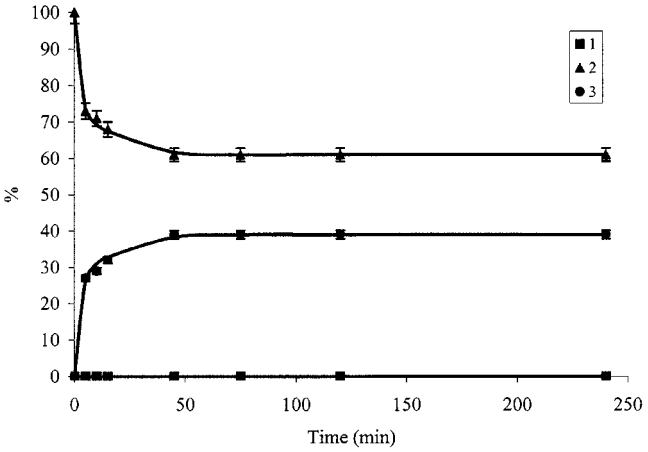


Figure 2. Diacetate proportions from **2** in THF

Partial loss of the olefin geometry can occur in the course of the Pd^0-catalyzed alkylation of *Z*-allylic acetates;[20] the general explanation is the generation of an η^3-allylpalladium intermediate having the sterically disfavored *anti*-form, its subsequent isomerization to the favored *syn*-η^3-allylpalladium intermediate through an $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$ interconversion and, finally, nucleophilic addition to this *syn*-intermediate.[1,2] If we consider a similar scheme for **1**, then the initial formation of complex **A** would lead to **D** via **B** and **C**. **B** and **C** are two conformers of the η^1-allyl complex and addition of the acetate anion at either the external or internal terminus of the allyl moiety of **D** would afford **2** and **3** respectively (Scheme 1, path *a*). However, since **D** should also be produced from **2** and **3**, the evolution of an equilibrium mixture of **2** and **3** should be observed from **1** (Figure 1) just as is observed when starting from pure **3** or pure **2** (Figure 2 and 3). Therefore, the results are clearly inconsistent with a mechanism involving solely **D** as the key species. While the results are in agreement with **D** mediating the 1,3-transposition of **2** and **3**, **D** cannot be the only intermediate when **1** is the substrate. Since in THF the acetate anion forms a tight ion-pair with cationic Pd-intermediates,[7] we propose that nucleophilic addition may also occur at the level of the ion-paired η^1-allylpalladium intermediate **C**, this process giving **2** exclusively through an S_N2' reaction (Scheme 1, path *b*).[21] Because **1** evolves more rapidly than **2** (cf. Figures 1 and 2), a high conversion of the former is attained before one observes 1,3-transposition of the latter, this taking place mainly after *t* = 15 min when the **2/1** distribution is ca. 85:15 (Figure 1). Consequently, after this point, the curves corresponding to the equilibration of **2** with **3** are similar to those observed in Figure 2.

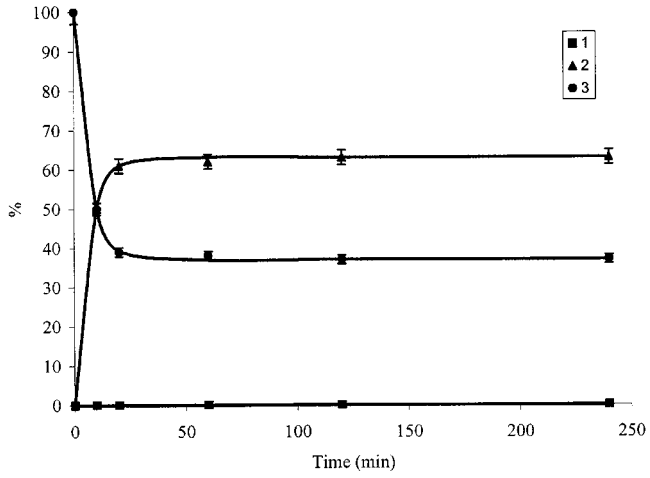
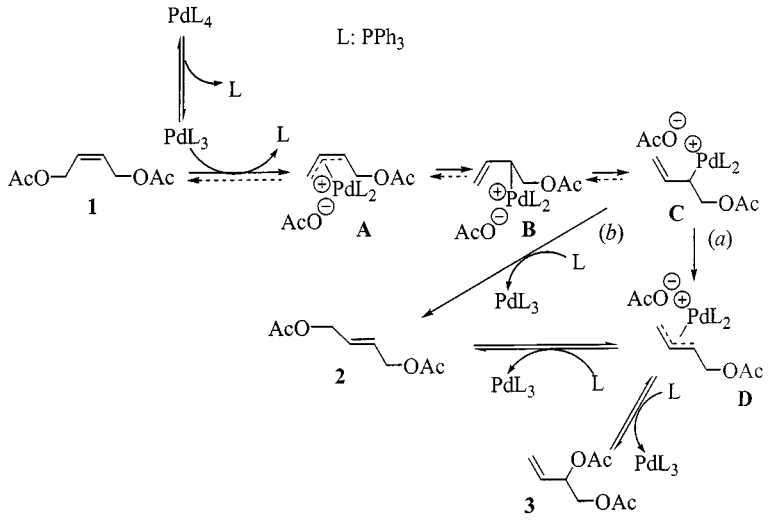


Figure 3. Diacetate proportions from **3** in THF

To test the proposition of the isomerization of **1** to **2** through an η^1- rather than an η^3-allyl complex in THF, the experiment was repeated using DMF, a polar solvent[22] in which free ions should be produced[7] (Figure 4, Table S4). As expected, the curves corresponding to the formation of **2** and **3** in Figures 1 and 4 are drastically different. As soon as the catalyst was added to the DMF solution of **1**, the simultaneous generation of **2** and **3** was observed. The ratio of **2/3** was constant (ca. 1.7) throughout the entire reaction, this being in full agreement with a reaction scheme in which **D** is the key intermediate. It is also interesting to note that



Scheme 1

the curves corresponding to the disappearance of **1** in Figures 1 and 4 are similar (see Figure S1 in the Supporting Information).

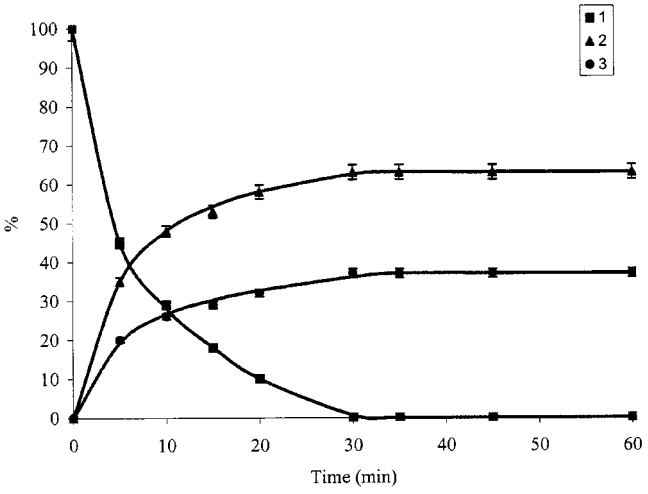
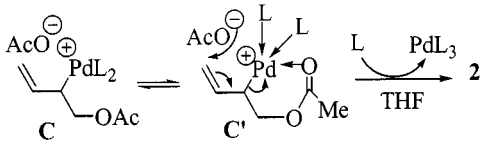


Figure 4. Diacetate proportions from **1** in DMF

Our results could have important ramifications for the Pd^0-catalyzed alkylation of allylic acetates and its enantioselective variant. In THF, the relative rates of reaction of η^3-allylpalladium intermediates — *anti*/*syn* isomerization, racemization, *cis*/*trans*-equilibration, retroreaction, alkylation — have been estimated;[23] the $\eta^1 \rightarrow \eta^3$ isomerization being particularly fast.[5] Therefore, the transformation of **C** to **2** must be rapid in THF since the generation of **D**, which corresponds to an $\eta^1 \rightarrow \eta^3$ isomerization, is not competitive. Furthermore, in addition to the effect of THF which, in **C**, maintains the acetate anion in close proximity to the allyl moiety, the ambidentate nature of the acetate anion could also contribute to its effective addition.[24] Moreover, instead of being a spectator, the other acetate group of the 14-electron complex **C** could act as an incipient ligand giving rise to a more stabilized complex **C′** possessing a 16-electron configuration (Scheme 2); this would decrease the electropositive character of the metal center. With **1** as substrate, the relative efficiency of some steps are strongly modified by a change of the polarity of the solvent; indeed, the similar rates of the disappearance of **1** in THF and DMF imply that the $\eta^1 \rightarrow \eta^3$ isomerization, which was ineffective in THF (**C** → **D**, Scheme 1, path *a*), competes effectively with the **C** → **2** step in DMF. A number of reports on the Pd-catalyzed enantioselective substitution of allylic acetates have described the dramatic dependence on the enantioselectivity with the nature of the solvent,[25,26] although the phenomenon is not general or predictable.[27−30] Among the various plausible origins of this solvent effect, such as interactions with the nucleophilic species and its counteranion[26] or with the chiral ligands, the possibility of a pronounced dependence on the "memory effect",[3−6] the reactive Pd-intermediates[31] and the efficiency of retroreactions with the medium polarity seems to have been underestimated. Hence, further investigation of the surprising and interesting phenomenon of the solvent effect on the mechanism and selectivity in Pd-catalysis is warranted.



Scheme 2

Experimental Section

THF was distilled from sodium/benzophenone under an argon atmosphere. Literature procedures were used for the preparation of $Pd(PPh_3)_4$.[32] (*Z*)-1,4-Diol-2-butene and (*E*)-1,4-dibromo-2-butene were used as received from suppliers. ^1H and ^{13}C NMR spectra were obtained with a Bruker AC 250 spectrometer in $CDCl_3$.

(*Z*)-1,4-Diacetoxy-2-butene (1):[33,34] Acetic anhydride (68 mL, 0.78 mol) was added in one portion to a stirred solution of (*Z*)-1,4-diol-

2-butene (19 mL, 0.23 mol) in dichloromethane (20 mL) at 0° under argon, followed by dropwise addition of pyridine (56 mL, 0.70 mol). After 30 min., the mixture was allowed to warm to room temperature and stirring continued for 18 h. The mixture was extracted with dichloromethane and the organic phase successively washed with 2 M HCl and saturated NaCl solution. After drying over magnesium sulfate and evaporation of the solvent, distillation led to **1** (34.5 g, 88% yield). b.p. 50 °C/0.05 mbar. – ^{1}H NMR: δ = 2.05 (s, 6 H, CH_3COO), 4.62 (d, J = 5.5 Hz, 2 H, OCH_2), 5.64 (m, 2 H, CH=CH). – ^{13}C NMR: δ = 20.5 (CH_3), 59.7 (OCH_2), 127.8 (CH=CH), 170.2 (C=O).

(*E*)-1,4-Diacetoxy-2-butene (2)[33–35]

Method A: A solution of (*E*)-1,4-dibromo-2-butene (5 g, 23.3 mmol) and potassium acetate (5 g, 51.0 mmol) in glacial acetic acid (20 mL) was refluxed for 24 h. After filtration of the resulting potassium bromide and evaporation of acetic acid, distillation provided **2** (3.2 g, 80% yield). b.p. 120 °C/21 mbar.

Method B: Adapted from a Z/*E*-isomerization procedure in the literature.[18,36] A solution of **1** (765 mg, 4.45 mmol) and PhSSPh (975 mg, 4.47 mmol) in cyclohexane (60 mL) was deoxygenated by bubbling with argon for 10 min. and then irradiated at λ > 290 nm for 3 h. After evaporation of the solvent, purification of the residue by flash chromatography led to **2** (617 mg, 81% yield). – ^{1}H NMR: δ = 2.06 (s, 6 H, CH_3COO), 4.58 (d, J = 5.5 Hz, 4 H, OCH_2), 5.85 (m, 2 H, CH=CH). – ^{13}C NMR: δ = 20.8 (CH_3), 63.9 (OCH_2), 128.1 (CH=CH), 172.0 (C=O).

1,2-Diacetoxy-3-butene (3):[34,35] Prepared from 1,2-diol-3-butene (3 g, 34.1 mmol) as described in the literature.[34] – ^{1}H NMR: δ = 2.07 (s, 3 H, CH_3COO), 2.10 (s, 3 H, CH_3COO), 4.07 (dd, J = 11.8, 7.2 Hz, 1 H, CH_2OAc), 4.22 (dd, J = 11.8, 3.8 Hz, 1 H, CH_2OAc), 5.26 (dt, J = 10.7, 1.1 Hz, 1 H, CH=CH_2), 5.31 (dt, J = 17.2, 1.1 Hz, 1 H, CH=CH_2), 5.49 (m, 1 H, CHOAc), 5.74 (ddd, J = 17.2, 10.7, 6.1 Hz, 1 H, CH=CH_2). – ^{13}C NMR: δ = 20.7 and 20.9 (2 CH_3), 64.7 (CH_2OAc), 72.0 (CHOAc 128.1 (CH=CH_2), 132.2 (CH=CH_2), 170.6 (C=O).

General Isomerization Procedure and Determination of the Acetate Ratios: Pd(PPh$_3$)$_4$ (0.168 g, 0.05 equiv.) was added to a solution of **1**, **2** or **3** (2.90 mmol) in dry THF or DMF (15 mL) under argon and the mixture was warmed in a bath heated at 70–72 °C. Samples were taken at the times reported in the tables and then filtered through Celite. After evaporation of the solvent and addition of TMS/CDCl$_3$, the ratios between the different acetates were established from the ^{1}H NMR spectra and the respective integrations of the CH_2 protons of **1** (δ = 4.62) and **2** (δ = 4.58) and the CH proton of **3** (δ = 5.74); the precision of the integrations was estimated to be ±3%.

Supporting Information Available: Tables S1–S4 and Figure S1 (see also footnote on the first page of this article).

Acknowledgments

Part of this work has been carried out in the framework of the COST D12/0028/99 program. We are grateful to Claire Thorey for preliminary experiments, to Engelhard Company for generous gifts of palladium salts and to G. Lloyd-Jones for help with the text of the manuscript.

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Received March 9, 2001
[O01117]