Short Review

Personal Observations on the Critical and Unusual Role of Palladium Environment on Reaction Pathways

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Abstract

This article summarizes some surprising palladoreactions occurring in a transition metal environment, discovered by our team, and the proposed corresponding mechanisms.

Keywords

Palladium; ethylenic bond; solvent; competing reaction pathways; mechanism; serendipity

1. Introduction

My interest in palladium in organic chemistry came from the reading of the 1977 Trost review [1] during my postdoctoral research in Corey's laboratory. Back to my Alma matter in late 1978, I was looking for new research subjects. My knowledge in photochemistry, acquired during my doctoral thesis [2], urged me to study the photoreactivity of η^3 -allylpalladium complexes. Having obtained 1,5-dienes from the UV light-mediated coupling of the allyl fragments in MeCN under the argon atmosphere [3], I undertook the preparation of squalene from *E,E*-farnesol [4]. This work led

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to my first observation of the critical role of an unreactive remote ethylenic bond in a palladoreaction. This unexpected observation was an incident of serendipity – that is by accident [5].

These studies were the outcome of forty-year research largely focused on palladium in organic chemistry. The initial topic was chosen, as I, unfortunately, was not aware of older papers from Hojabri who only observed the decomposition of the η^3 -allylpalladium complex of β -pinene under UV irradiation in EtOH, without dimerization of the allyl ligands or effect of oxygen [6, 7]. Actually, we observed, under an oxygen atmosphere, the oxidation of the allyl moieties into conjugated carbonyl compounds [8, 9] even in EtOH [10].

The above role of a remote ethylenic bond and other unexpected results due to the Pd environment, which we observed over the years, are the matter of this short review.

2. Remote Ethylenic Bond

2.1 Allylpalladium Isomerization

Using the preparation procedure of bis(μ -chloro)bis(η^3 -allyl)dipalladium complexes [11-13], I treated *E,E*-farnesyl chloride (**1**) with substoichiometric amounts of $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ in benzene at room temperature. Surprisingly, a 1:1 mixture of syn- and anti- η^3 -allylpalladium complexes¹ **2a** and **2b** was isolated (Figure 1) [4]. Suspecting the possible role of one of the remote C=C bonds of **1** in the formation of the mixture, geranyl (**3**), neryl (**4**), and phytol (**5**) chlorides were treated under the same conditions. A 1:1 mixture of **6a** and **6b** was obtained from **3** and **4**, while **7a** (**7a/7b** > 9)² was selectively produced from **5**. RMN studies of the excess of allylic chlorides **3** and **4** recovered at the end of the reactions showed that they were not isomerized under the experimental conditions. Stirring the solution of **7a** with a large amount (≈ 1000 equiv.) of cyclohexene or 2-methylbut-2-ene led only to very poor isomerization at room temperature. Then, a 6:4 mixture of **7a** and **7b** was isolated from the reaction of **5** with $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ in the presence of 100 equiv. of 2-methylbut-2-ene.

Figure 1 Allylic chlorides and corresponding η^3 -allylpalladium complexes.

¹ For the meaning of syn- and anti-η³-allylpalladium complexes, see [14, 15].

² Mistake in [4]: the **8a/8b** value is > 9 instead of 0.9. In the present review, **7a** and **7b** correspond to **8a** and **8b** of the original paper.

According to the above experiments, the formation of the syn and anti mixtures is promoted by the intra- or intermolecular participation of an isolated C=C bond. Isomerization preceding the formation of the dimeric complex is suspected. This could occur via the $\eta^3\text{-}\eta^1\text{-}\eta^3$ equilibrium of monomeric allylpalladium intermediates [16] having an ethylenic bond as a ligand (Figure 2).

Figure 2 The $\eta^3\text{-}\eta^1\text{-}\eta^3$ equilibrium.

Subsequently, Åkermark's team rediscovered the formation of the isomeric η^3 -allylpalladium complex mixture from geranyl and neryl chlorides [17, 18], while Rovis and Johnson provided an overview of olefins influencing the outcome of various reactions [19].

2.2 Oxidation Inhibition

In 1995, we disclosed the oxidation of alcohols using catalytic amounts of both PdCl_2 and Adogen 464³ in 1,2-dichloroethane (DCE) containing sodium carbonate [20]. The insoluble palladium dichloride reacts with ammonium salt to yield the soluble palladium salt $[\text{PdCl}_4]^{2-}$ [21], which further oxidizes the alcohol. The resulting reduced Pd species gets inserted into a C-Cl bond of DCE. Subsequent elimination of ethylene regenerates the active catalyst [20, 22]. Using the procedure for the lactonization of 1,4- and 1,5-diols, we surprisingly obtain the formation of lactol **9u_{exo}** from *cis-endo*-2,3-bis(hydroxymethyl)bicyclo[2.2.1]hept-5-ene (**8u**) although *cis-endo*-2,3-bis(hydroxymethyl)bicyclo[2.2.1]heptane (**8s**) provided lactone **10s** (Figure 3) [23, 24]. Furthermore, **9u_{exo}** was almost unchanged under the same experimental conditions without production of **10u**, whereas the latter was effectively produced from **9u_{exo}** using pyridinium dichromate in CH_2Cl_2 (Figure 3) [25, 26] or by the Swern oxidation method [27]. Moreover, our Pd procedure led to the effective oxidation of lactol **11** into the corresponding lactone [24].

³ Adogen 464 is a registered trademark of Ashland Chemical Co. for methyltrialkyl(C8-C10)ammonium chloride.

Figure 3 Oxidation of **8u**, **8s**, **9u_{exo}**, **11** and **13**.

The above results clearly demonstrated that the lack of formation of **10u** from **8u** under Pd-conditions was attributable to the C=C bond. In order to explain this unusual role, we considered the plausible intermediates of the process (Figure 4; the absence of a juxtaposed u or s letter as suffix to compound numbers of Figure 4 and corresponding text means that these numbers correspond indifferently to either the unsaturated or the saturated substrate.). Hydroxyaldehyde **HAd** may be in equilibrium with lactols **9_{exo}** and **9_{endo}** and may react with [PdCl₄]²⁻ to give alkoxypalladium aldehyde **PAd**. The low reactivity of aldehyde **13** under the reaction conditions (Figure 3) is not in favor of the formation of hydroxyacid **HAc** from **HAd**⁴. Furthermore, unsaturated **HAcu** is expected to spontaneously generate lactone **10u** [29, 30], which, in fact, was not produced from the Pd-catalyzed reaction of **8u**. The pallado-intermediates, **P9_{exo}** and **P9_{endo}**, may be produced from **9_{exo}** and **9_{endo}** (path *b*) or **PAd** (path *a*). Subsequent β-H elimination would afford **10**, but this only occurs for the formation of **10s**.

Figure 4 Oxidation of **8u** and **8s**; plausible intermediates.

⁴ Formation of ester **14** from **13** involves the acid as intermediate [28].

The analysis of the literature led us to reject some hypotheses⁵ and to propose that (i) palladation of **HAd** (path *a*) is preferred over that of lactols (path *b*), and (ii) the intramolecular reaction of **PAd** occurs through the stereoselective approach of the alkoxypalladium moiety to one face of the aldehyde to afford **P9_{endo}**. When the latter is obtained from **8s**, the β -H elimination easily occurs to deliver **10s**. In contrast, **P9_{endo}** obtained from **8u** undergoes a ligand exchange leading to palladacycle **PCu** (Figure 5). The syn relationship between O-Pd and C-H bonds, which would allow the β -H elimination leading to the carbonyl unit [31, 32], is prevented in **PCu**. That favors alkoxyde exchange with diol **8u** to afford **9u_{endo}**. The latter evolves towards **9u_{exo}** which is a more stable isomer [33-35].

Figure 5 Role of the C=C bond in the formation of lactol **9u_{exo}**.

The apparent absence of **9u_{exo}** evolution under the aforementioned Pd-catalyzed reaction conditions is a “no reaction” reaction [36, 37], which involves **HAdu**, **9u_{endo}**, **PCu**, alcoholysis and equilibration regenerating the starting substrate.

3. Oxidation Versus Etherification

The above catalytic Pd procedure is efficient for the oxidation of 1-indanol (**15**) into 1-indanone (**16**) [20]. We obtained a similar result using the soluble palladium salt synthesized from PdCl₂ and *n*-Bu₄NCl instead of the PdCl₂/Adogen 464 association (Figure 6, path *a*) [21, 38]. Surprisingly, soluble (RCN)₂PdCl₂ produced di(1-indanyl) oxide (**17**) at a high yield, even in the absence of the base (Figure 6, path *b*) [38].

Figure 6 Influence of the Pd environment on the reaction pathways of 1-indanol.

⁵ See discussion and references in [24].

We rationalized the formation of **16** and **17** through two competitive pathways catalyzed by L_2PdCl_2 ($L = Cl^-$ or RCN), i.e., with $[PdCl_4]^{2-}$ and $(RCN)_2PdCl_2$, respectively (Figure 7) [38]. In contrast to the anionic catalyst ($L = Cl^-$), the neutral catalyst ($L = RCN$) is electrophilic [39-42]. The exchange of ligand between L_2PdCl_2 and **15** affords **7A**. The evolution of **7A** depends on the electrophilicity of L_2PdCl_2 . Transition metals having Lewis acid properties mediate the formation of ethers from alcohols [43, 44]. Consequently, **7A** formed from the anionic catalyst evolves toward **16** via the ketonization pathway [20, 22], while **7A** formed from $(RCN)_2PdCl_2$ undergoes heterolytic cleavage of the C-OH bond leading to the ionic species **7B**. The latter reacts with **15** to give ether **17**, water and the starting catalyst.

Figure 7 Pathways leading to either oxidation or etherification of 1-indanol.

4. Solvent-Mediated Pathways

4.1 Halide Exchange Versus Alkylation

As pointed out in the introduction of the present discourse, the irradiation of a bis(μ -chloro)bis(η^3 -allyl)dipalladium complex in deoxygenated MeCN leads to the allyl coupling. Thus, the *l*-carvone complex **18** provided **19** (Figure 8, path *a*) [3]. Then, we looked for different photoreactions [45]. Having observed the lack of photoreactivity of **18** in CH_2Cl_2 in the absence of additive, this solvent was firstly chosen for reactions in the presence of organic halides. Halogen-exchanged complexes **20** were thus isolated (Figure 8, path *b*). Changing CH_2Cl_2 for DMF^6 , the reaction with benzyl bromide led to a 1:1 mixture of allylic alkylation and allyl coupling products **21** and **19**, respectively (Figure 8, path *c*). These results showed that the species able to temporarily coordinate to palladium, such as MeCN or DMF, are required to form the C-C bonds under these irradiation conditions. In fact, we obtained the results similar to those in DMF when the photolysis in CH_2Cl_2 was carried with PPh_3 as an additive (Figure 8, path *c*). The analysis of these reactions by EPR (electron paramagnetic resonance) [51] and CINDP (chemically induced dynamic nuclear polarization) [52] spectroscopies demonstrated their radical character.

⁶ For the multi-roles of DMF in chemistry, see [46-50].

Figure 8 Dependence of the photoreactivity of η^3 -allylpalladium complex **18** on the environment.

4.2 η^1 - Versus η^3 -Allylpalladium

Our synthesis of enantiopure vinylmorpholines by the Pd^0 -catalyzed diastereoselective disubstitution of (*Z*)-1,4-diacetoxy-2-butene (**22**) with chiral amino alcohols in THF [53] urged us to examine the isomerization of the substrate [54]. Golding's team briefly reported that treatment of **22** with catalytic $\text{Pd}(\text{PPh}_3)_4$ in PhH at room temperature gave (*E*)-1,4-diacetoxy-2-butene (**23**) [55]. At 70–72°C in THF, we obtained a mixture of **23** and 1,2-diacetoxy-3-butene (**24**). The two compounds were also produced in DMF. Monitoring these reactions by ^1H NMR resulted in unexpected observations. While **23** and **24** were produced in DMF at a constant **23/24** ratio, the latter varied with time in THF (Figure 9). After 15 min, the amount of **23** decreased to afford the **23/24** equilibrium, indicating that, in THF, **24** was mainly produced from **23** rather than from **22**. Subsequent treatments of **23** and **24** with $\text{Pd}(\text{PPh}_3)_4$ in THF showed an equilibrium between them. According to these results, the isomerization of **22** occurs as depicted in Figure 10 [54].

Figure 9 Isomerization of **22** (dark line) into **23** (red line) and **24** (blue line) using $\text{Pd}(\text{PPh}_3)_4$ (0.05 equiv.) at 70–72°C in DMF or THF.

Figure 10 Formation of **23** and **24** according to monitoring analysis.

Allylpalladium intermediates with the $\eta^3\text{-}\eta^1\text{-}\eta^3$ mechanism were proposed for the *Z/E*-isomerization and the 1,3-transposition of allylic acetates [56]. The proposed reaction pathways of **22** was based on the demonstration given by Amatore and Jutand about the influence of solvent on the species formed from allyl acetate, $\text{Pd}(\text{dba})_2$ and PPh_3 : “in THF, the acetate ion sticks on the palladium(II) complex (ion pair)” while “in DMF (free ions), the acetate is located far from the cationic η^3 -allylpalladium(II) center” [57, 58]. The reaction of **22** with the catalyst leads to cationic η^3 -allylpalladium intermediate **11A** that is in equilibrium with the η^1 -allyl palladium species **11B** (Figure 11). The rotation around the AcOC-C(allyl)Pd bond gives **11C** that may afford either **23** by nucleophilic addition of the acetate anion to the external terminus of the allyl group, or η^3 -allylpalladium complex **11D**. The latter may also be formed from **23**. **11C** being a tight ion-pair in THF, the close proximity of the acetate anion with the allyl moiety favors the efficient addition leading to **23**. Whereas in DMF, the separation of the two entities favors the formation of **11D**. The latter evolves toward **23** and **24**.

Figure 11 Dependence on the solvent of isomerization intermediates.

$\text{Pd}(\text{PPh}_3)_4$ -catalyzed isomerization of (*Z*)-1-(*t*-butyldimethylsilyloxy)-4-acetoxy-2-butene and (*Z*)-1-(*t*-butyldiphenylsilyloxy)-4-acetoxy-2-butene led to similar results [59]. Different intermediates have been proposed for the Pd^{II} -catalyzed isomerization of **22**, **23** and **24**, and the role of the environment of palladium due to THF or DMF on the reactivity has also been highlighted [60].

4.3 Selectivity

While only allyl alcohol **25** and allyl ether **26** were obtained in the presence of acetylacetonate (**acacH**) from the reaction of 1-acetoxy-1,3-diphenylpropene (**27**) in MeOH under basic conditions, the addition of H₂O provided a 55:40 mixture of **26** and the cross-coupling product **28** (Figure 12, paths *a* and *b*, respectively) [61]. Thus, water may promote a Tsuji-Trost-type reaction under metal-free conditions. The selectivity in **28** was strongly increased (Figure 12, path *c*) [62] by catalytic amounts of both (MeCN)₂PdCl₂ and the highly hydrophilic ligand **L_H** (Figure 13) that we previously used for Cu-catalyzed allylic acetoxylations in water [63]. Repeating the reaction in the absence of water dramatically decreased the yield of the Tsuji-Trost adduct with the production of the compounds obtained in MeOH under metal-free conditions (Figure 12, path *d*). Thus, water also promotes the Pd catalyzed addition of **acacH** to **27**.

Figure 12 Dependence of selectivity on the presence of water.

Figure 13 A water-soluble ligand.

ESI-MS (electrospray ionization mass spectrometry) analysis of these reactions led us to assume the possibility of in situ formation of palladium acetylacetonate complex **29** and the absence of η^3 -allylpalladium intermediates (Figure 14) [62]. As a result, it was proposed that **29**, which would be a more effective nucleophile than **acacH** and MeOK, reacts with the water-activated substrate. The efficient recycling of the catalyst [62] showed that a Pd^{II} complex is truly immobilized in water, and led to assume the production of water-coordinated palladium species such as **30** as intermediates of the catalytic cycle.

Figure 14 Formation of a Tsuji-Trost product without η^3 -allylpalladium intermediate.

5. Conclusion

The above examples highlight the unexpected observations made in the course of our studies, on the effect of the palladium environment on the outcome of reactions. Of course, several critical roles of the palladium environment have also been documented in the literature. These influences on the reactivity have attracted tremendous attention toward palladium in organic chemistry. New reactions and mechanisms are often serendipitously discovered but nevertheless, in most cases, they are the outcomes of deep investigations and reflections rather than good fortune [5].

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Author Contribution

Jacques Muzart did the whole writing of the review.

Competing Interests

The author has declared that no competing interests exist.

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