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Elimination of β-palladium hydroxide in the Pd^{II}-catalyzed reaction of methyl (α-hydroxymethyl)acrylate with alcohols

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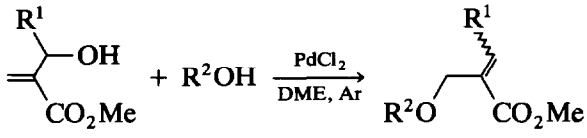
Abstract

Exclusive elimination of β-Pd–OH takes place in the oxypalladation intermediate derived from methyl (α-hydroxymethyl)acrylate and alcohols with $PdCl_2$ catalyst, and no β-Pd–H elimination occurs.

Key words: Palladium; Hydroxide; Catalysis; Alkene; Mechanism

Oxypalladation towards terminal olefinic carbon of allylic alcohols with $PdCl_2$ produces σ-bonded palladium(II) species bearing a hydroxy group at the β-position which generally undergoes facile elimination of β-Pd–H to give aldehydes (Scheme 1) [1]. Recently, it was reported that allyl alcohol itself, when treated with methanol in the presence of excess LiCl, gives allyl methyl ether which arises formally via elimination of Pd–OH [2]. The alternation of the reaction pathways has been justified in view of the stabilization of the oxypalladation intermediate by external Cl^-. Thus, excess Cl^- prevents formation of the labile coordination site on Pd^{II} necessary for elimination of Pd–H, resulting in reverse deoxypalladation (Scheme 1). In this context, we report here a new observation that the oxypalladation of allylic alcohols bearing a COOR group at the 2-position undergoes exclusive elimination of β-Pd–OH even in the absence of LiCl, and that alternative β-Pd–H elimination is entirely suppressed. This result sheds light on the mechanism of the reactions formally involving elimination of β-Pd–OH [3–5].

In the course of our study on the Pd(II)-catalyzed acetalization of alkenes with alcohols [6], we found that the reaction of methyl (α-hydroxymethyl)acrylate (**1a**, R = H) with MeOH (5 equiv) in the presence of $PdCl_2$ catalyst (10 mol%) (DME, 50°C, Ar) gives ether **2a** exclusively in 77% yield (eqn. (1)). In this reaction, no aldehyde was formed.

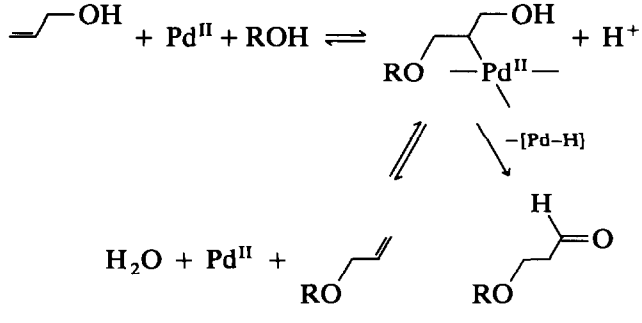


(1)

2

1	**a**; R^1 = H,	R^2 = Me
a; R^1 = H	**b**; R^1 = H,	$R^2 = CD_3$
b; R^1 = Me	**c**; R^1 = H,	R^2 = Et
c; R^1 = Ph	**d**; R^1 = H,	$R^2 = PhCH_2$
	e; R^1 = Me,	R^2 = Me

The following experiments prove that the reaction proceeds via nucleophilic attack of ROH on the π-



Scheme 1.

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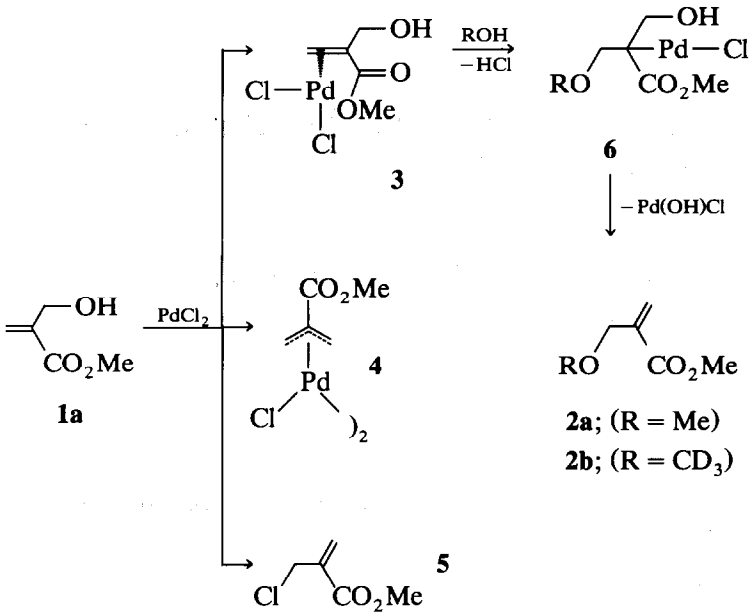


Scheme 2.

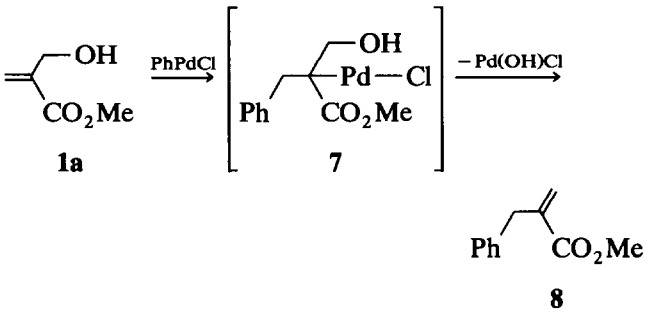
complex **3** followed by elimination of Pd–OH as shown in Scheme 2. A solution of **1a** and $PdCl_2(CH_3CN)_2$ (both 0.077 M) in $CDCl_3$ at 50°C in a sealed tube was subjected to ^{1}H-NMR measurement, and the progress of the reaction was monitored. After 5 days, the spectrum showed three sets of new peaks corresponding to π-complex **3** (29%), η^3-allyl complex **4** (19%), and methyl (α-chloromethyl)acrylate (**5**) (8%) (Scheme 2), respectively. At this stage, 44% of unreacted **1a** remained. The structure of the π-complex **3** was assigned by the following observations. The ^{1}H spin-lattice relaxation time constants (T_1) of the olefinic protons in **3** are faster (around 2 s at 35°C) than the 4.2 s for those of uncomplexed **1a**. A low mobility of ligands upon complexation has been known to decrease the T_1 values [7], and indeed the protons of η^3-allyl complex **4** show smaller T_1 values (around 2 s). The olefinic protons in **3** appear in lower chemical shifts ($\Delta = \sim 0.06$ ppm) relative to those of **1a**, indicating the π-complexation of Pd(II). Furthermore, irradiation at the methyl proton of COOMe group in **3** induces a nuclear Overhauser effect on the olefinic proton located in the position *syn* to the COOMe group. These observations allow us to assign one set of new peaks to appear as the π-complex **3** [8*].

When CD_3OD (5 equiv to **1a**) was added to the above solution, the complex **3** and unreacted **1a** were gradually converted into **2b** ($R = CD_3$), and finally all the peaks of **3** and **1a** were changed to those of **2b** (62%, 95 h). However, the η^3-allyl complex **4** and (α-chloromethyl)acrylate (**5**) remained intact. This result clearly indicates that the ether **2a** (or **2b**) is formed by elimination of Pd–OH from intermediate **6** derived from the π-complex **3**, and that neither the species **4** nor the compound **5** is the precursor of ether **2a** (or **2b**) [9*]. Of course, the vinyl ether or the aldehyde, expected to arise from **6** by elimination of β-Pd–H, is not detected among the products. Of note is that the use of acids such as *p*-toluenesulfonic acid in place of Pd^{II} catalyst does not induce the reaction.

The reaction is susceptible to the steric bulkiness of alcohols and substrates **1**, because the reaction requires π-complexation of the olefin and subsequent nucleophilic attack of alcohols. Thus, ethanol or benzyl alcohol reacts with **1a** rather slowly, giving the corresponding ether **2c** (69%, 50 h) or **2d** (62%, 96 h) (eqn. (1)). Introduction of methyl substituent at 3-position of the alkene **1a** retards the reaction (**2e**: 48% for 92 h, E/Z = 31/69). No reaction takes place with **1c** bearing phenyl substituent at the 3-position.

For further confirmation of the elimination of Pd–OH, the allylic alcohol **1a** was subjected to a Heck reaction [10]. Thus, the reaction of **1a** with PhPdCl,

* Reference number with asterisk indicates a note in the list of references.



Scheme 3.

prepared from $PdCl_2$ and PhHgCl in CH_2Cl_2 at room temperature, afforded methyl (α-phenylmethyl)acrylate (**8**) (32%) which arises from the σ-bonded palladium intermediate **7** by elimination of β-Pd–OH (Scheme 3). In this case, 3-phenyl-2-carbomethoxyproinoaldehyde derived from elimination of β-Pd–H from **7** was formed in 21% yield. However, the treatment of allyl alcohol itself with PhPdCl under similar conditions gives 3-phenylproinoaldehyde exclusively via a process involving elimination of β-Pd–H [11].

There are only a few precedents for elimination of β-Pd–OH, and the present result is unique in terms of inhibition of facile elimination of β-Pd–H as well as a proof of the occurrence of elimination of β-Pd–OH in the oxypalladation reaction of allylic alcohols. Reactions involving σ-bonded Pd(II) intermediates of cyclic structures, such as tetrahydrofurans, which bear no β-hydrogen to Pd, have been known to include elimination of β-Pd–OH [3,4]. However, in such cases, there is no possibility of *cis* β-Pd–H being eliminated. In the present system, suppression of competitive elimination of β-Pd–H appears to reflect the fact that none of the four hydrogen atoms β to Pd in **6** (Scheme 2) can occupy the position *cis* to Pd which is necessary for elimination of β-Pd–H. Such a situation is probably attained by coordination of the palladium to both oxygen atoms of the OH and ester carbonyl.

References and notes

1 K. Zaw, M. Lautens and P.M. Henry, *Organometallics, 2* (1983) 197; *Organometallics, 4* (1985) 1286; W.K. Wan, K. Zaw and P.M. Henry, *Organometallics, 7* (1988) 1677.

2 C.M. Dumiao, J.W. Francis and P.M. Henry, *Organometallics, 10* (1991) 1400.

3 U. Hacksell and G.D. Daves, Jr., *Organometallics, 2* (1983) 772; S. Saito, T. Hara, N. Takahashi, M. Hirai and T. Moriwake, *Synlett*, (1992) 237.

4 J.W. Francis and P.M. Henry, *Organometallics, 11* (1992) 2832.

5 S. Ma and X. Lu, *J. Organomet. Chem., 447* (1993) 305.

6 T. Hosokawa, T. Ohta, S. Kanayama and S.-I. Murahashi, *J. Org. Chem., 52* (1987) 1758; T. Hosokawa and S.-I. Murahashi, *Acc. Chem. Res., 23* (1990); T. Hosokawa, T. Yamanaka and S.-I. Murahashi, *J. Chem. Soc., Chem Commun.*, (1993) 117.

7 R.J. Abraham and P. Loftus, *Proton and Carbon NMR Spectroscopy*, Heyden, London, 1978, p. 130; J-E. Bäckvall and A. Gogoll, *Tetrahedron Lett., 29* (1988) 2243.

8 The other two sets of peaks corresponding to η^3-allyl complex **4** and methyl (α-chloromethyl)acrylate (**5**) were assigned by comparing the NMR data with those of authentic samples. The chemical shifts observed are as follows: δ 6.31 (dt, $J = 1.5$ and 1.3 Hz, 1H), 5.90 (dt, $J = 1.5$ and 1.7 Hz, 1H), 4.25 (dd, $J = 1.7$ and 1.3 Hz, 2H), and 3.76 (s, 3H) for π-complex **3**; δ 4.65 (s, 2H), 3.89 (s, 3H), and 3.25 (s, 2H) for (η^3-allyl)palladium(II) complex **4**; δ 6.38 (dt, $J = 0.9$ and 0.5 Hz, 1H), 5.98 (dt, $J = 0.9$ and 1.3 Hz, 1H), 4.28 (dt, $J = 1.3$ and 0.5 Hz, 2H), and 3.81 (s, 3H) for compound **5**.

9 The compound **5** is also formed via chloropalladation towards **1a** followed by elimination of β-Pd–OH.

10 R.F. Heck, *Palladium Reagents in Organic Syntheses*, Academic Press, London, 1985, pp. 268–276.

11 R.F. Heck, *J. Am. Chem. Soc., 90* (1968) 5526; see also Jeffery, *Tetrahedron Lett., 32* (1991) 2121; R.C. Larock, W-Y. Leung, and S. Stolz-Dunn, *Tetrahedron Lett., 30* (1989) 6629 and references cited therein.