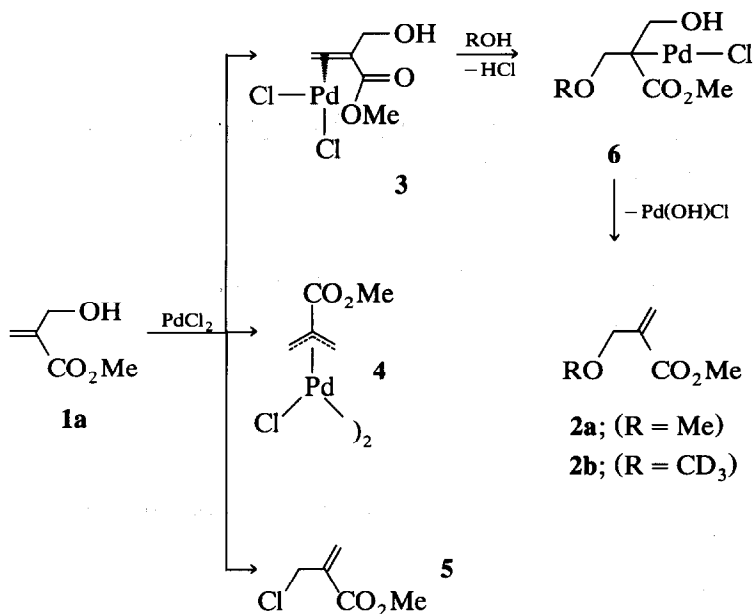




Scheme 2.

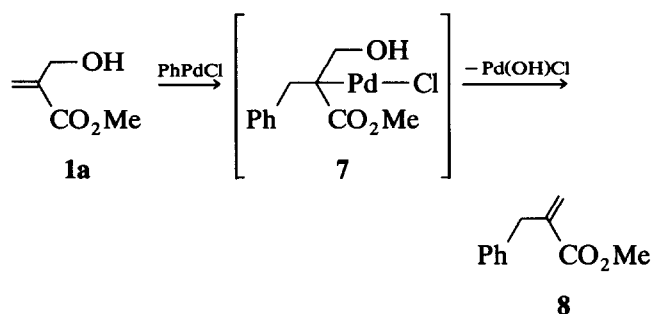
complex **3** followed by elimination of Pd-OH as shown in Scheme 2. A solution of **1a** and PdCl₂(CH₃CN)₂ (both 0.077 M) in CDCl₃ at 50°C in a sealed tube was subjected to ¹H-NMR measurement, and the progress of the reaction was monitored. After 5 days, the spectrum showed three sets of new peaks corresponding 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 ¹H 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*].

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

When CD₃OD (5 equiv to **1a**) was added to the above solution, the complex **3** and unreacted **1a** were gradually converted into **2b** (R = CD₃), 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,



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

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- 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.
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