Palladium(II)-catalysed Oxidative Cyclisation of 2-Allylphenols in the Presence of Copper(II) Acetate and Molecular Oxygen. Oxidation State of Palladium in the Wacker-type Reaction

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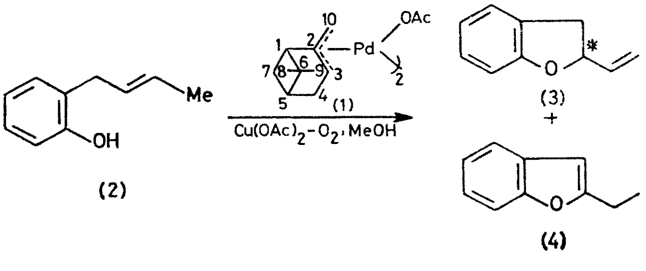
Summary In the catalytic oxidative cyclisation of 2-(but-2-enyl)phenol (**2**) by (+)-[(3,2,10-η-pinene)PdOAc]$_2$ (**1**) in the presence of Cu(OAc)$_2$ and O$_2$, the η^3-pinene ligand in (**1**) remains attached to palladium throughout the reaction, an observation which cannot be accounted for by the conventional Wacker-type catalysis.

The oxidative cyclisation of 2-allylphenols by palladium(II) is an intramolecular version of the Wacker reaction.[1] The Pd^{II} in the Wacker reaction is reduced to Pd^0 and hence reactions of this type are not catalytic. In catalytic reactions where Cu^{II} and O$_2$ are used, the role of these reagents has been frequently described as in equations (1) and (2);[2] in these reactions the reoxidation of Pd^0 is accomplished by the redox system Cu^{II}–Cu^I. Thus, it has been

$$\mathrm{Pd^0 + 2CuX_2 \longrightarrow Pd^{II}X_2 + 2CuX} \qquad (1)$$

$$\mathrm{2CuX + 2HX + \tfrac{1}{2}O_2 \rightarrow 2CuX_2 + H_2O} \qquad (2)$$

widely believed that the oxidation state of palladium in the Wacker-type catalysis changes as follows: Pd^{II} → Pd^0 → Pd^{II}. We report here that the oxidation state of palladium in the catalyst (+)-[(3,2,10-η-pinene)PdOAc] (**1**) does not change in this manner during the oxidative cyclisation of 2-allylphenols in the presence of Cu(OAc)$_2$ and O$_2$. This finding throws light on a new aspect of the Wacker-type catalysis.



Scheme 1

The cyclisation of 2-(but-2-enyl)phenol (**2**) in the presence of (**1**), Cu(OAc)$_2$, and O$_2$ (Scheme 1) gives optically active (*S*)-(+)-2-vinyl-2,3-dihydrobenzofuran (**3**) along with 2-ethylbenzofuran (**4**).[3] The optical rotation of (**3**) formed does not change with reaction time (Table). This indicates that the optically active η^3-pinene species is retained as a ligand in (**1**) throughout the reaction. However, it is not possible to account for this by assuming a catalytic cycle for (**1**) as shown in equations (3)—(7), *i.e.*, (i) the cyclisation proceeds by intramolecular oxypalladation with loss of AcOH followed by Pd–H elmination to give (**3**) and (**4**) [equation (3)],[4] (ii) the resulting (η^3-pinene)Pd–H decomposes to Pd^0 and pin-2(10)-ene [equation (4)], and (iii) the subsequent reactions are of the conventional

Table

Reaction time[a]/h	Yield of (**3**) + (**4**)[b]/%	Ratio[c] of (**3**):(**4**)	$[\alpha]_D^{25}$ of (**3**)[d]
3·5	21	69:31	+3·30
4·5	32	76:24	+3·45
4·7	41	80:20	+3·42
5·0	64	84:16	+3·36
6·0	82[e]	85:15	+3·42

[a] Reaction was performed by using 0·05 M of (**1**), 0·5 M of (**2**), and 0·5 M of Cu(OAc)$_2$ (anhydrous) in absolute MeOH at 35 °C under O$_2$ (*ca.* 1 atm). [b] Yield was determined by g.l.c. with internal standard, unless otherwise noted. [c] Ratio of area of g.l.c. peak. [d] Measured in CCl$_4$, after preparative g.l.c.; the optical yield of (**3**) is calculated to be *ca.* 14% (ref. **3**). [e] Isolated yield.

$$\mathbf{(2)} + \tfrac{1}{2}\,\mathbf{(1)} \longrightarrow \mathbf{(3)} + \mathbf{(4)} + (\eta^3\text{-pinene})\text{PdH} + \text{AcOH} \tag{3}$$

$$(\eta^3\text{-pinene})\text{PdH} \longrightarrow \text{pin-2(10)-ene} + \text{Pd}^0 \tag{4}$$

$$\text{Pd}^0 + 2\text{Cu(OAc)}_2 \longrightarrow \text{Pd(OAc)}_2 + 2\text{CuOAc} \tag{5}$$

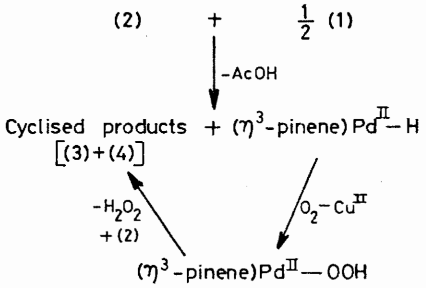
$$2\text{CuOAc} + 2\text{AcOH} + \tfrac{1}{2}\text{O}_2 \rightarrow 2\text{Cu(OAc)}_2 + \text{H}_2\text{O} \tag{6}$$

$$\text{pin-2(10)-ene} + \text{PdOAc)}_2 \rightarrow \tfrac{1}{2}\,\mathbf{(1)} + \text{AcOH} \tag{7}$$

$$\mathbf{(2)} + \tfrac{1}{2}\text{O}_2 \longrightarrow \mathbf{(3)} + \mathbf{(4)} + \text{H}_2\text{O}$$

Wacker-type catalysis [equations (5) and (6)] and **(1)** is rapidly formed by the reaction of pin-2(10)-ene with Pd(OAc)$_2$ alone [equation (7)].† Our attempt to obtain support for the reaction in equation (4) from the following independent experiment failed. When **(2)** was treated with a stoicheiometric amount of **(1)** [**(2)**:Pd = 1:1] in the absence of Cu(OAc)$_2$ and O$_2$, (−)-pin-2-ene **(5)** and (+)-3,4-dihydropin-2(10)-ene **(6)** (44:55 by g.l.c.) were formed along with **(3)**, **(4)**, and metallic Pd, but pin-2(10)-ene was not obtained in any significant amounts. Therefore, equations (3)—(7) do not provide a rational explanation of the results shown in the Table. Furthermore, **(5)** or **(6)** cannot be the source of chirality in the parent reaction, because **(5)** did not induce chirality in **(3)**,[3] and **(6)** ($[\alpha]_D^{20}$ + 85·5, MeOH) gave rise to (*R*)-(−)-**(3)** ($[\alpha]_D^{20}$ −1·65, CCl$_4$), the configuration of which is opposite to that of the product of the parent reaction.

In the stoicheiometric reaction of **(2)** with **(1)** the rate of cyclisation is very slow (*ca.* 170 h for 50% completion) when both O$_2$ and Cu(OAc)$_2$ are absent. Although the rate increases slightly by introduction of O$_2$, the presence of both O$_2$ and Cu(OAc)$_2$ accelerates the reaction remarkably (6.5 h for >99% completion). Under these conditions, 50% of the unchanged starting complex **(1)** is recovered after completion of the cyclisation. These results indicate that a highly active palladium species, which is different from the original complex **(1)**, is formed in the presence of O$_2$ and Cu^{II}. Since the Wacker reaction generally generates a Pd–H species,[5] the active species in our reaction may be Pd–OOH formed by the reaction of Pd–H and O$_2$ and, for the oxygenation of Pd–H, Cu^{II} presumably serves as a transient oxygen carrier. A catalytic cycle for the reaction reported here can thus be described as shown in Scheme 2 where the optically active η^3-pinene ligand is retained by the catalyst during the reaction. Although further studies are necessary in order to elucidate the role of Cu^{II} and O$_2$ in reactions of this type, it is clear that the results presented in this communication cannot be accounted for by the conventional Wacker-type catalysis.



Scheme 2

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† Pin-2(10)-ene, when treated with 1 equiv. of Pd(OAc)$_2$ in MeOH for 5 min, yielded the complex **(1)** quantitatively.

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