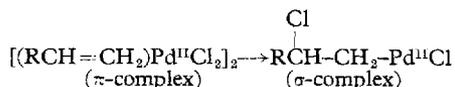


# The Use of Palladium Compounds in Organic Synthesis

## CARBONYLATION OF UNSATURATED MOLECULES

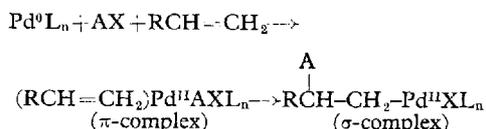
Until the discovery of the Wacker reaction – the palladium-catalysed oxidation of ethylene to acetaldehyde – some ten years ago, the only application of palladium in organic synthesis was as a hydrogenation catalyst. In more recent years a number of new reactions have been found to be catalysed solely by palladium and its compounds, especially interesting reactions being those in which new carbon to carbon bonds are formed by the insertion of carbon monoxide into unsaturated molecules.

Salts and complexes of divalent palladium, Pd<sup>II</sup>, are well known to have the ability of co-ordinating molecules having one or more olefinic double bonds, the species formed being referred to as a  $\pi$ -complex (1, 2). As a result of co-ordination, the chemical reactivity of the olefin is greatly altered: normally prone only to electrophilic attack (e.g., by H<sup>+</sup> or Br<sup>+</sup>), it becomes susceptible to nucleophilic attack by anions, with a consequent widening of the scope of synthetic reactions based on olefins. The general sequence of events is as follows: a ligand already present on the palladium attacks the co-ordinated olefin, forming a  $\sigma$ -bonded species containing a carbon-palladium bond which is highly reactive. It is at this stage that insertion reactions, for example with carbon monoxide, may be performed. In the final decomposition of this species, the palladium is usually reduced to zero valent palladium, Pd<sup>0</sup>, and so the process is not catalytic unless the Pd<sup>0</sup> is immediately reoxidized to Pd<sup>II</sup>.



Pd<sup>0</sup> complexes suitably stabilised with *n* molecules of a ligand *L* also act as catalysts for olefin addition reactions since they may be reversibly oxidised by a molecule of AX to

the Pd<sup>II</sup> state, the resulting  $\pi$ -complex then rearranging to the  $\sigma$ -complex as above:

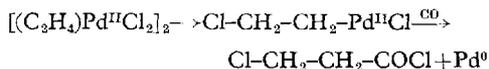


This  $\sigma$ -complex may decompose to yield RCH(A)-CH<sub>2</sub>X, regenerating Pd<sup>0</sup>L<sub>*n*</sub>.

One of the leading figures in this area of synthetic chemistry, Dr J. Tsuji, of the Toyo Rayon Company of Japan, has recently surveyed its present status (3), and this review owes much to him.

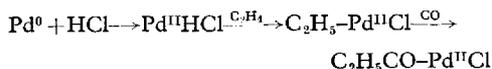
### Carbonylation of Olefins

Carbon monoxide reacts at room temperature with the  $\pi$ -complex, ethylene palladous chloride, in benzene to yield  $\beta$ -chloropropionyl chloride:



When the reaction is performed in ethanol, the chlorine atoms are solvolysed and the product is C<sub>2</sub>H<sub>5</sub>O-CH<sub>2</sub>-CH<sub>2</sub>-COOC<sub>2</sub>H<sub>5</sub>, ethyl  $\beta$ -ethoxypropionate. If, however, the reaction is performed at 100°C using metallic palladium and ethanol acidified with HCl, the product is CH<sub>3</sub>-CH<sub>2</sub>-COOC<sub>2</sub>H<sub>5</sub>, ethyl propionate. The reason for the difference is quite simply that the  $\sigma$ -complex or alkyl-

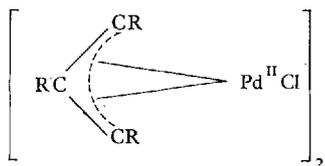
palladium complex results from olefin insertion into the H-Pd bond, not the Cl-Pd bond:



The acyl complex formed by CO insertion then decomposes to  $\text{C}_2\text{H}_3\text{COCl}$  which is subsequently solvolysed to the observed product.

### Carbonylation of $\pi$ -Allylic Complexes

It is also well known that with olefins having the structure  $\text{R}_2\text{C}=\text{CR}-\text{CHR}_2$  (where R may be H or any alkyl or substituted alkyl group) there may be formed with palladous chloride by elimination of HCl a complex in which all three carbon atoms are bonded equally to the palladium atom: such a species is known as a  $\pi$ -allylic complex (1, 2) and is represented as:



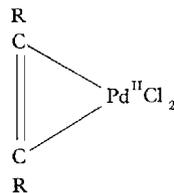
The C-Pd bonds are again quite reactive and the complex may be carbonylated at  $100^\circ\text{C}$ : the above complex (having  $\text{R}=\text{H}$  throughout) yields  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{COCl}$ , 3-butenoyl chloride, when the reaction is conducted in benzene and predictably ethyl 3-butenolate if ethanol is the solvent. As the products are still capable of forming  $\pi$ -allylic complexes, it is possible to repeat the process and obtain diethyl glutaconate,  $\text{C}_2\text{H}_5\text{OCO}-\text{CH}_2-\text{CH}=\text{CH}-\text{COOC}_2\text{H}_5$ .

The carbonylation of conjugated dienes and of allenes may also be carried out, but when the  $\pi$ -allylic complex is not symmetrical there are two possible places for attack by carbon monoxide and a complex mixture of products results.

### Carbonylation of Acetylenes

Molecules containing acetylenic triple bonds also form complexes with palladous chloride,

the product being represented as:



Acetylene reacts with carbon monoxide in the presence of solutions of palladous halides, the iodide being particularly effective (4); the products which are observed result from the insertion of either one or two molecules of carbon monoxide. Thus in *n*-butanol the products are the *n*-butyl esters of acrylic acid ( $\text{H}_2\text{C}=\text{CH}-\text{COOH}$ ) and propionic acid ( $\text{CH}_3-\text{CH}_2-\text{COOH}$ ) and the di-*n*-butyl esters of fumaric and maleic acids ( $\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ : maleic is the *cis*-isomer, fumaric the *trans*-isomer) and of succinic acid ( $\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{COOH}$ ) (4).

Many aspects of the mechanism of carbonylation of unsaturated molecules remain to be studied. Although the unsaturated molecule must be co-ordinated to the palladium atoms it is uncertain whether the carbon monoxide molecule must be simultaneously co-ordinated or not; Tsuji appears to think this unnecessary, but the reaction is more plausibly interpreted as a *cis*-ligand transfer, a type of process for which there are very many examples in the field of homogeneous catalysis.

These reactions are specific to palladium and its compounds and are not readily achieved with other metals. Furthermore, palladium and its effective compounds are easily handled and are stable especially towards oxidation, unlike many complexes of the noble metals which have been used as homogeneous catalysts. Finally, the processes in question can often be made catalytic by reoxidation of  $\text{Pd}^0$  as in the Wacker process (2).

### References

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- 2 G. C. Bond, *Platinum Metals Rev.*, 1964, 8, 92
- 3 J. Tsuji, *Accounts Chem. Res.*, 1969, 2, 144
- 4 R. Long and C. B. Lines, *Abstr. Papers, 157th Mtg, Am. Chem. Soc.*, 1969 (Apr.), PETR 52