# The Mechanism of Formation of π-Allylic Palladium(II) Chlorides from Sodium Chloropalladite, Allylic Chlorides, and Carbon Monoxide Reacting in Aqueous Methanol

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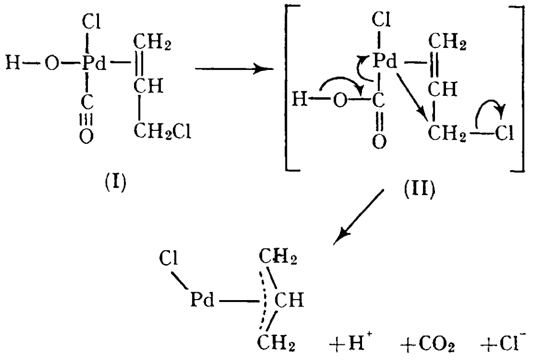
RECENTLY there has been great interest in the study of allylic complexes of transition metals particularly in bridged halogeno-π-allylic complexes of palladium(II).[1,2] Of several methods of preparing these palladium complexes undoubtedly the best is that due to Dent, Long, and Wilkinson[3] who found that passage of carbon monoxide through an aqueous methanolic solution of sodium chloropalladite containing allyl chloride produced an almost quantitative yield of π-allylpalladium chloride, $[Pd_2Cl_2(C_3H_5)_2]$.

From other allylic chlorides we have similarly prepared excellent yields of a variety of π-allylic palladium(II) chloride complexes. Dent *et al.*[3] did not suggest a mechanism for the reaction nor explain the part played by the carbon monoxide but found that in methanol the yield was poor. In view of its preparative importance we have investigated the reaction more fully and find that *ca.* one molecule of carbon monoxide is oxidised to carbon dioxide per palladium atom and suggest that water is directly involved.

The following mechanism is proposed (for simplicity not all the ligands are shown)—



Allyl chloride, carbon monoxide, and water co-ordinate to the palladium but since co-ordinated water is quite acidic {*e.g.*, the species $[PtCl_2(H_2O)(C_2H_4)]$, formed by hydrolysis of Zeise's salt $K[PtCl_3C_2H_4]$, has an acid dissociation constant of *ca.* $10^{-5}$ [4]} some of the hydroxo-species (I) will be formed. Hydroxyl migration (or carbon monoxide insertion) then gives the carboxylate complex (II) which breaks down as shown to give hydrochloric acid, carbon dioxide, and $\pi$-allylpalladium chloride (monomer which them dimerises). Carbon monoxide has been shown to insert itself between a metal–oxygen bond by Schoeller *et al.*[5] and Halpern and Kettle[6] who found that mercuric acetate and carbon monoxide reacted in methanol solution to give $[AcOHgCO_2Me]$. Harkness and Halpern[7] also postulated the ion $[HgCO_2H]^+$ as a key intermediate in the oxidative hydrolysis of carbon monoxide to carbon dioxide by mercuric ions.

We are currently investigating the oxidative hydrolysis of other substituted metal carbonyls and feel that the reaction will prove useful for the synthesis of other types of organometallic complexes.

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