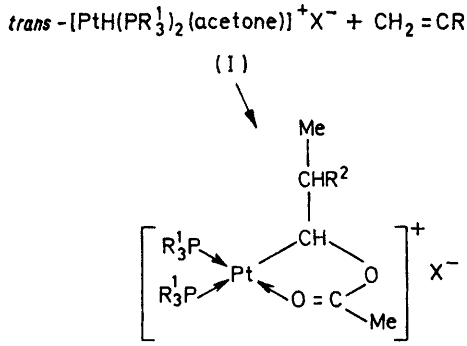
The Mechanism of Formation of Propionaldehyde and π-Allylplatinum(II) Complexes from Allyl Alcohol and Diallyl Ether with Cationic Platinum(II) Hydrides

By H. C. Clark* and H. Kurosawa

(*Department of Chemistry, University of Western Ontario, London, Canada*)

Summary Migration of the C=C bond and chelate ring formation occur in the insertion reactions of allylic acetates with cationic platinum(II) hydrides; similar behaviour explains the formation of π-allylplatinum(II) complexes and propionaldehyde from reactions of allyl alcohol or diallyl ether with such cationic hydrides.

Homogeneous isomerization of olefins, catalysed by platinum(II) complexes, was thought[1] to proceed *via* insertion into a platinum–hydrogen bond. We have previously discussed[2] the importance of the cationic intermediates, *trans*-$[PtH(PR_3)_2(olefin)]^+$ in the ready insertion of olefins into the Pt–H bond, and we now describe the reactions of some allylic compounds with *trans*-$[PtH(PR_3)_2(acetone)]^+$ X^- (I). The reaction shown in equation (1) occurs readily at room temperature to give platinum(II)-alkyl complexes apparently derived from isomers of the original allylic reactants.



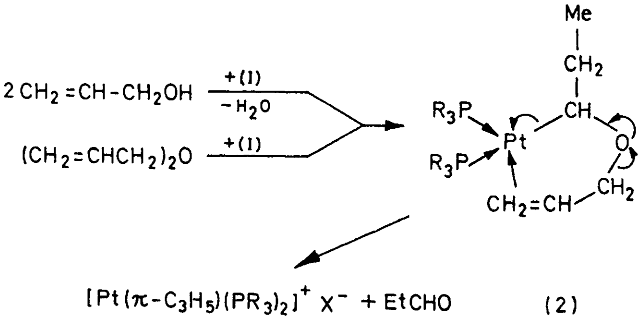
(1)

(II)

(IIa) $PR^1_3 = PPh_2Me$, $R^2 = H$, $X = BF_4$

(IIb) $PR^1_3 = PPh_2Me$, $R^2 = Me$, $X = BF_4$

(IIc) $PR^1_3 = PPh_3$, $R^2 = H$, $X = ClO_4$



(2)

(III)

The structure of (II) was deduced from elemental analyses and i.r. and ^1H n.m.r. data. The lowering of $\nu(C{=}O)$ to 1575 from 1755 cm^{-1} is consistent with the proposed co-ordination of the carbonyl group to platinum. $J(Pt\text{–}PMe)$ for (IIa,b) is 52 and 15 Hz respectively, which is in agreement with the postulated structure, since these coupling constants are dependent on the ligand *trans* to the phosphine.[3] The isolation of (II) is particularly interesting since the formation of a similar chelate structure has been proposed[4] to explain the formation of ethylidene diacetate from ethylene and acetic acid with palladium(II) chloride.

Compound (I) also reacts with either 2 mol. equiv. of allyl alcohol or 1 mol. equiv. of diallyl ether at room temperature to give equimolar amounts of propionaldehyde and (III) ($R_3 = Ph_2Me$ or Ph_3, $X = BF_4$; $R_3 = Ph_3$, $X = ClO_4$). We have previously obtained[2] the complexes (III) by the reaction of (I) with allene. The formation of propionaldehyde from allyl alcohol with a Ru^{III} or Rh^{III} catalyst,[5] as well as with $Fe(CO)_5$[6] or $HCo(CO)_4$,[7] and of the π-allylpalladium(II) complex from allyl alcohol and palladium(II) chloride[8] have been reported previously, but the course of the present reactions is obviously different. The reactions of (I) with allyl alcohol and diallyl ether probably proceed *via* the sequence shown in equation (2), involving both the migration of the double bond and chelate ring formation. Complexes of type (III) were also prepared by the reaction of (I) with allylamine or allyl bromide, and the mechanisms of these reactions are currently being investigated.

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