

## Reactions of Platinum(II)-stabilised Carbonium Ions

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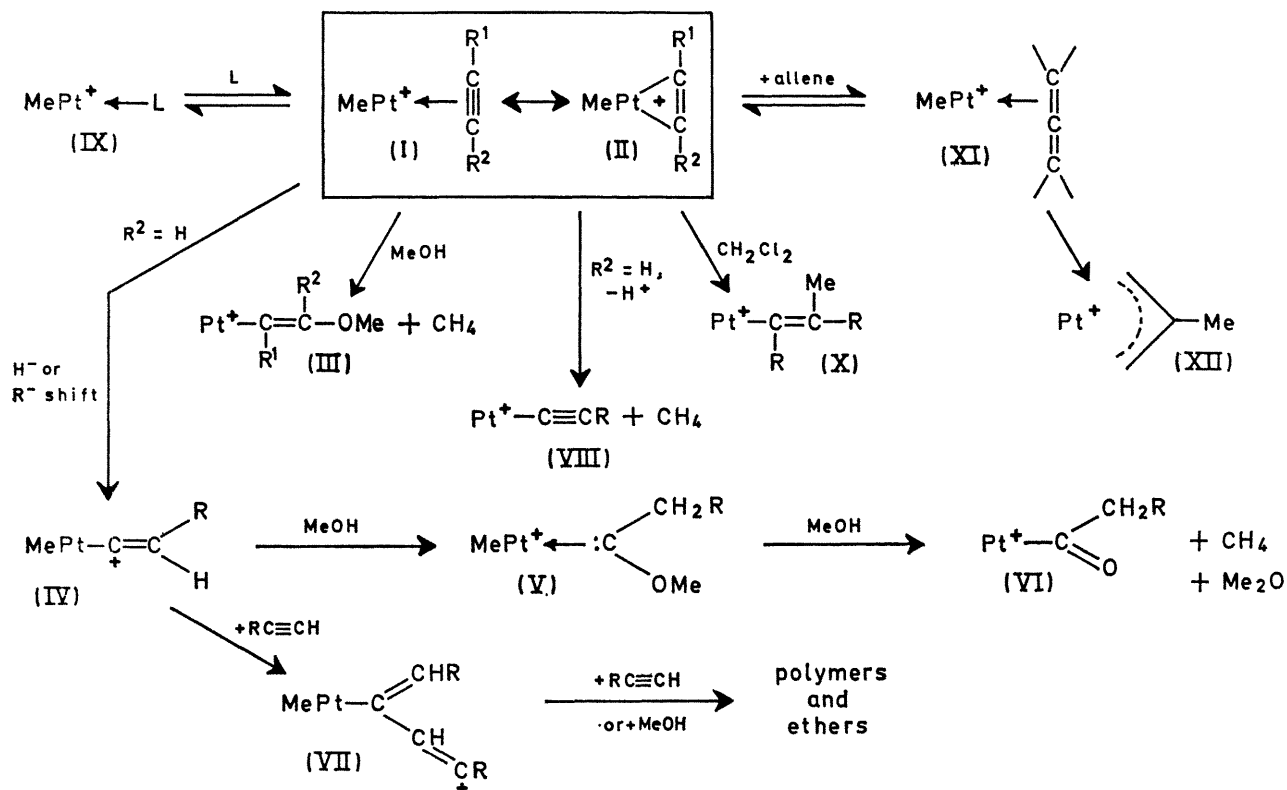
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**Summary** Complexes  $trans\text{-}[\text{PtMe}(\text{L})\text{Q}_2]^+\text{PF}_6^-$  ( $\text{Q} = \text{PMe}_2\text{-Ph}$  or  $\text{AsMe}_3$  and  $\text{L} =$  an acetylene or allene) show reactivity characteristic of carbonium ions and lead to a variety of products by intramolecular rearrangements and/or nucleophilic addition.

THE reaction of methanolic solutions of  $trans\text{-PtClMeQ}_2$  ( $\text{Q} = \text{PMe}_2\text{Ph}$  or  $\text{AsMe}_3$ ) with acetylenes  $\text{R}^1\text{C}\equiv\text{CR}^2$  and silver hexafluorophosphate gave cationic acetylene, acetylide, methoxycarbene or methyl vinyl ether complexes

$trans$ -addition was first predicted<sup>5</sup> by analogy with the behaviour of bromonium ions.

The anti-Markownikov addition of methanol to the acetylene to give the methoxy-carbene complexes (V) occurs by rearrangement of (II) to the platinum-stabilised carbonium ion (IV). Acyl formation, which takes place more slowly, results from further nucleophilic attack by methanol on (V). Ratios of monoalkyl acetylenes to  $trans\text{-PtClMeQ}_2$  in excess of 1:1 increase the yields of organic "tars" at the expense of (V) and (VI). We consider



**SCHEME.** Some reactions of  $trans\text{-}[\text{PtMe}(\text{R}^1\text{C}\equiv\text{CR}^2)\text{Q}_2]^+\text{Z}^-$  ( $\text{Q} = \text{PMe}_2\text{Ph}$  or  $\text{AsMe}_3$ ;  $\text{Z} = \text{PF}_6$  or  $\text{Cl}$ ) (I) [ $\text{Z} = \text{PF}_6$ ,  $\text{R} =$ alkyl or aryl (ref. 1, 2)], (III) ( $\text{Q} = \text{PMe}_2\text{Ph}$ ,  $\text{R}^1 = \text{R}^2 = \text{CO}_2\text{Me}$ ,  $\text{CO}_2\text{H}$ ,  $\text{CH}_2\text{OH}$ , or  $\text{Me}$ ), (V) [ $\text{Z} = \text{PF}_6$ ,  $\text{R} = \text{H}$  or alkyl (ref. 1, 2)], (VI) ( $\text{Z} = \text{Cl}$ ,  $\text{Q} = \text{PMe}_2\text{Ph}$ ,  $\text{R} = \text{H}$  or  $\text{Me}$ ), (VIII) ( $\text{Z} = \text{PF}_6$ ,  $\text{Q} = \text{AsMe}_3$ ,  $\text{R} = \text{Ph}$ ), (IX) ( $\text{Z} = \text{PF}_6$ ,  $\text{Q} = \text{PMe}_2\text{Ph}$ ,  $\text{L} = \text{PR}_3$ ,  $\text{AsR}_3$ ,  $\text{CO}$ ,  $\text{RCN}$ ,  $\text{L} =$ olefins, allene, acetone), (XI) and (XIII) ( $\text{Z} = \text{PF}_6$ ,  $\text{Q} = \text{PMe}_2\text{Ph}$ ). The ligands  $\text{Q}$  have been omitted in the scheme for brevity. Satisfactory analytical data have been obtained for all compounds not previously reported.

depending on the nature of the acetylene.<sup>1,2</sup> Even in the absence of silver hexafluorophosphate certain acetylenes react *via* cationic acetylenic intermediates to give acyl or vinyl ether derivatives. Some reactions of methylplatinum-acetylene complexes (I) are shown (see Scheme).

The stability (and reactivity) of (I) is dependent on  $\text{R}^1$  and  $\text{R}^2$  and only when these are alkyl or aryl groups has (I) been isolated. (I) may be considered as the platinum-stabilised carbonium ion (II) and this readily explains the susceptibility to nucleophilic attack. The formation of vinyl ether complexes (III) is stereospecific with *trans*-addition to the triple bond and may be compared to many metallation reactions, *e.g.* the oxymercuration of olefins<sup>3,4</sup> for which

that the excess of acetylene provides an alternative nucleophile for reaction with (IV) [or (II)] thus leading *via* (VII) to polymerisation and a variety of organic products.

Formation of the acetylide (VIII) presumably arises because the acidity of the acetylenic proton in  $\text{RC}\equiv\text{CH}$  is greater for  $\text{R} = \text{Ph}$  than for  $\text{R} =$ alkyl,<sup>6</sup> and so proton elimination, (II)  $\rightarrow$  (VIII), is more favourable than  $\text{R}^-$  shift, (II)  $\rightarrow$  (IV).

Nucleophilic attack on (I) may occur at the platinum atom thus giving (IX) by displacement of the acetylene or an equilibrium between (I) and (IX) depending on the basicity of the nucleophile (see Scheme).

A study of the reactions of (I) in non-nucleophilic solvents

has been made possible by the isolation of (IX) (L = acetone) since acetone is readily displaced by acetylenes, olefins, and allenes in chlorinated solvents. Acetylenes with electron-withdrawing substituents such as  $\text{CF}_3$  give cationic vinyl complexes (X) in which *cis*-addition to the triple bond occurs, *cf.* the *trans*-addition, (II)  $\rightarrow$  (III), in methanol. The reaction of (IX) (L = acetone) with allene in dichloromethane gives the  $\pi$ -2-methylallyl cation (XII) at room temperature, which is analogous to the  $\pi$ -allyl formation recently reported<sup>7</sup> in the reaction of a cationic hydridoplatinum complex with allene. However, below 0° the  $\pi$ -allene complex (XI) may be obtained quantitatively. N.m.r. studies show that the conversion of (XI) into (XII) is independent of the concentration of (XI), thus supporting

an intramolecular rearrangement [as in (II)  $\rightarrow$  (X)]. The bonding in transition metal allene complexes is of current interest.<sup>8-10</sup> Variable temperature n.m.r. studies, 0 to -60°, of (XI) show that the allene is co-ordinated to platinum through *only* one of the  $\pi$ -bonds (no fluxional behaviour is observed) and that rotation about this bond is restricted below -20°, consistent with the adoption of a preferred conformer in which the allene is perpendicular to the  $\text{MePtP}_2$  plane.

Many transition metal-catalysed reactions of olefins and acetylenes may proceed by mechanisms analogous to those indicated in the scheme. These will be discussed elsewhere.

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