Some New Platinum Acetylene Complexes

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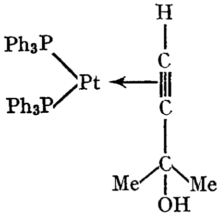
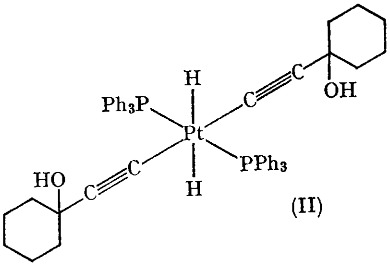
ACETYLENE complexes of platinum have been known for many years. The most common method of co-ordination is by a π-bond with the bond order of the acetylene reduced to approximate closely that of an olefin.[1] Recently, however, the reaction between perfluoropropynemagnesium bromide and bis(triphenylphosphine)platinum dichloride has been found to give a bisacetylide complex.[2] In the dimerisation of 1-hydroxyacetylenes by tris(triphenylphosphine)rhodium(I) chloride, the postulated intermediateis a rhodium acetylide hydride complex formed by insertion of the metal into the acetylenic carbon–hydrogen bond.[3]

We report the reactions of two 1-hydroxyacetylenes with tetrakis(triphenylphosphine)platinum(0). With 3-methylbut-1-yn-3-ol a colourless crystalline complex is obtained of stoicheiometry $(PPh_3)_2PtCMe_2OH{\cdot}C{\equiv}CH$. The i.r. spectrum of the compound shows bands due to triphenylphosphine, an O–H stretch at 3620 cm.$^{-1}$, and a band at 1710 cm.$^{-1}$ due to a π-bonded acetylene. The structure (I) is further confirmed by the ^{1}H n.m.r. spectrum which shows four resonances at τ 2·78(30), 8·42(1), 8·47(1), and 8·70(1) due to the phenyl, hydroxyl, acetylenic, and methyl protons respectively. The hydroxyl and acetylenic protons signals were assigned by the addition of D_2O to the solution which caused the lower field line to collapse, identifying it as the hydroxyl.



(I)



(II)

The position of the acetylenic proton signal in the n.m.r. is noteworthy. In the free acetylene it is observed at τ 7·52, whereas in the complex it is at τ 8·47, representing an upfield shift of 0·95 p.p.m.

The reaction with 1-ethynylcyclohexanol again produces a colourless crystalline complex, but this compound has the stoicheiometry $(PPh_3)_2Pt(C_8H_{12}O)_2$. When dry this new complex is air stable but it decomposes when heated in solution or on the addition of alcohol, to give a yellow product which has not been investigated.

The i.r. spectrum shows a band due to the O–H stretch at 3620 cm.$^{-1}$ and bands due to triphenylphosphine. There are no bands in the 1500—2000 cm.$^{-1}$ region but there is a strong band at 2120 cm.$^{-1}$. In the pure acetylene the C=C stretch occurs weakly at 2117 cm.$^{-1}$, and this band in the complex could be due to either $\nu(-C{\equiv}C)$ or ν(Pt–H).

The ^{1}H n.m.r. spectrum of the complex shows three resonances. The two lower field ones consist of unresolved multiplets centred at τ 2·39(5) and 9·05(4) due to the phosphine and methylenic protons, the relative areas confirming the 1 : 1 triphenylphosphine ligand ratio. The third resonance occurs at τ 32·88 and can only be due to a metal hydride.

The spectral data indicates a structure (II) for the complex which is a Pt^{IV} acetylide hydride. The structure should be octahedral with the phosphines *trans* to each other.

The n.m.r. spectrum shows no separate resonance due to the hydroxy-group, because this proton has shifted upfield into the methylene region, this shift being in the anticipated direction since the concentration of the hydroxy-group is less in a solution of the complex than in the pure acetylene.

The marked difference in structure between these two complexes is also shown by their mass spectral breakdown patterns. Complex (I) shows strong peaks for the breakdown pattern of the ligand, as expected for a π-bonded moiety. However, for complex (II) the peaks for the dissociated acetylene could not be identified and this complex shows only the breakdown pattern for triphenylphosphine. The spectrum shows three weak peaks at 196, 197, and 198 which are the PtH_2 fragments for the three isomers of platinum, and the relative strengths of the peaks are in close agreement with the isotopic abundance of platinum.

We thank Dr. N. S. Bhacca of Louisiana State University for assistance with the n.m.r. spectra, Dr. W. Carpenter of the U.S. Naval Weapons Research Centre for assistance with the mass spectral data, and the Esso Research Laboratories, Louisiana, for financial assistance.

(*Received, July* 25*th*, 1968; *Com.* 1002.)

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