The Formation of Palladium(II)- and Platinum(II)-Carbon Bonds by Proton Abstraction from Benzo[*h*]quinoline and 8-Methylquinoline

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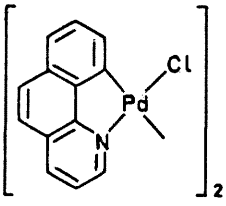
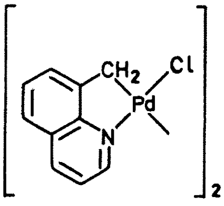
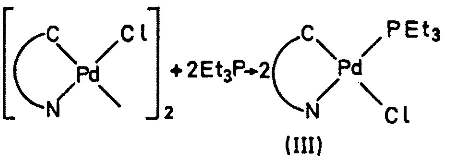
Summary The preparation of complexes containing palladium(II)- and platinum(II)-carbon bonds by proton abstraction from planar quinoline ligands, excludes a π-arene complex as a necessary intermediate during formation and presents the first examples of this reaction to include alkylprotons.

HALOGEN-BRIDGED dimeric complexes of palladium(II) and platinum(II) containing metal–carbon bonds have been prepared by proton abstraction from azobenzene,[1] *NN*-dimethylbenzylamines,[2] *N*-benzylideneanilines,[3] *NN*-dimethyl-1-naphthylamine,[3] and 2-phenylpyridine.[4] In each case the hydrogen is abstracted from an *ortho*-aryl position and a five-membered ring is formed. Recently a mechanism for such intramolecular aromatic substitution processes was suggested to include, as an intermediate step, a π-arene complex.[5]

Using benzo[*h*]quinoline and 8-methylquinoline, we have prepared the new dimeric complexes (I) and (II) through a proton-abstracting process. The yellow complexes are prepared by stirring 2 equiv. of the quinoline in methanol with 1 equiv. of lithium tetrachloropalladate(II) in water until the red colour of the tetrachloropalladate ion disappears. Analytical samples of the complexes, which are nearly insoluble in common organic solvents, were obtained through continuous extraction with dichloromethane or toluene.


(I)


(II)


(III)

The bridged dimers are easily cleaved by a stoicheiometric amount of triethylphosphine in benzene. The structure of the four-co-ordinate complexes produced is drawn (III) to agree with that recently suggested for a similar series of palladium compounds prepared by the same reaction.[6] The n.m.r. spectrum of the 8-methylquinoline complex in deuteriochloroform does show the methylene protons, τ 6·88, as a doublet, J_{PH} 4 Hz, in agreement with *trans*-bromobenzylbis(triethylphosphine)palladium(II).[7] However, the proton *ortho* to the ligand nitrogen is also coupled to the phosphorous, J_{PH} 5 Hz, τ 0·42. I.r. and Raman spectra of these compounds do not allow a definite assignment of structure at this time, and studies of the bromine analogues are in progress.

The two ligands are unique in that their planarity will not allow the formation of a π-arene complex prior to abstraction, thus such an intermediate complex is not a prerequisite in the mechanism of the formation of the metal–carbon bond. In addition, the 8-methylquinoline complex is the first example of abstraction from an alkyl rather than an aryl proton in this type of ligand.

The corresponding 8-methylquinoline complex of platinum has also been prepared and will even form in the presence of an excess of HCl. In contrast, 2-phenylpyridine and benzo[*h*]quinoline with HCl yield pyridinium and quinolinium salts of the tetrachloroplatinate anion.

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