

Reactions of Primary Amines and Acetate Ion with Platinum and Palladium Alkadiene Halide Complexes

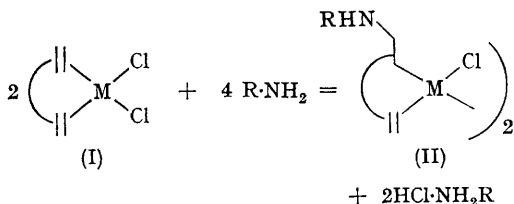
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[(Diene)MX₂] (I), where M is platinum or palladium, react with alkoxides,¹ β-diketones,² and ethyl malonate³ giving complexes containing M-C σ-bonds. The stereochemical pattern of the oxyplatination and oxypalladiation reaction⁴ and the stereospecific reaction of an optically active co-ordinated diolefin with a racemic alcohol mixture⁵ have been reported.

We have found that complexes of type (I), M = Pt or Pd, diene = cyclo-octa-1,5-diene, norbornadiene, 4-vinylcyclohexene, and hexa-1,5-diene, react with primary amines and the acetate ion in a similar way.

With primary amines [*e.g.*, benzylamine, (S)-α-phenylethylamine] the reaction goes quantitatively at room temperature in different solvents (*e.g.*, acetone, methanol, dichloromethane) according to the equation:



to form compound (II), which is also obtained with one equivalent of amine in the presence of sodium carbonate.

† The formula represents composition only.

‡ [4-vinylcyclohexene-PdCl₂] has been obtained by the reaction of 4-vinylcyclohexene and Na₂PdCl₄ in CHCl₃ at room temperature, as yellow crystals, m.p. 128–130° (decomp.).

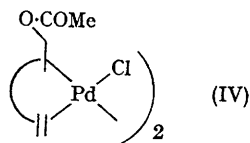
Products (II) with benzylamine, are crystalline white-yellow solids, dimeric, and moderately soluble in dichloromethane. They react with triphenylphosphine to form the complexes, [(diene)(amine)M(Ph₃P)Cl],† (III), which are monomeric and nonconducting in nitrobenzene.

Analysis, i.r. and n.m.r. spectra, and the cryoscopic molecular weight of complexes (II) and (III) are consistent with our formulation. On decomposition with aqueous KCN it is possible to recover the corresponding free olefins.

On reduction of (II) with hydrogen a secondary amine is obtained (*e.g.*, reduction with H₂ at 1 atm. of [norbornadiene-(S)-(α-phenylethylamine)-PdCl₂]₂† suspended in ethyl ether, gives as the major component a secondary amine; the elemental analysis, i.r. and n.m.r. spectra are consistent with the formula C₇H₁₁NHC₈H₉).

A similar compound [strictly related to the postulated intermediates in palladium(II) catalyzed formation of vinylic ester] was obtained through the reaction between [4-vinylcyclohexene-PdCl₂]₂† and sodium acetate in methanol.

A crystalline pearly product is obtained which may be formulated as



on the basis of the analysis, n.m.r. and i.r. spectra. Reduction of (IV) with hydrogen gives 1-cyclohexylethyl acetate, identical with an authentic sample (v.p.c. analysis and i.r. spectra).

Detailed mechanism and stereochemical aspects of these reactions, with optically active amines are at present in progress.

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