INTRAMOLECULAR AMINOPALLADATION REACTION OF 1-AMINOHEXATRIENE

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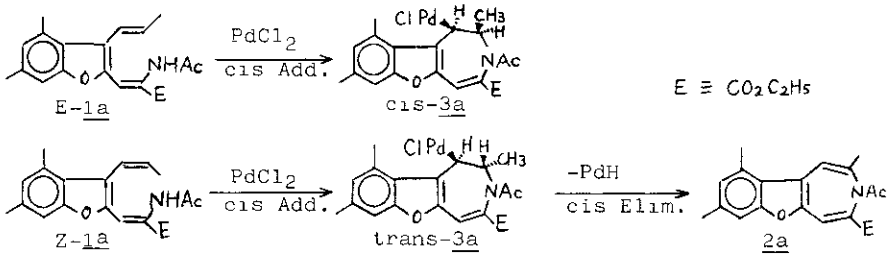
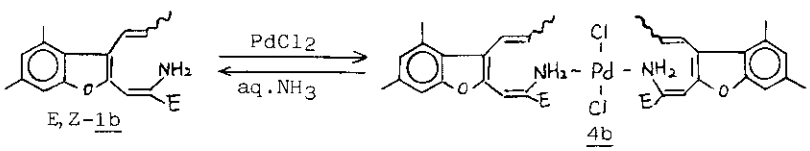
We have recently found palladium promoted formation of azepines from 1-amino-hexatrienes. In order to investigate this reaction in more detail, we performed aminopalladation reactions of several 1-aminohexatrienes.

When Z-isomer of N-acetylaminohexatriene Z-1a was treated with 1 eq. of $PdCl_2(PhCN)_2$ in acetonitrile in the presence of Na_2CO_3, the azepine 2a was obtained. However, in the case of its E-isomer E-1a palladium-σ-complex, cis-3a was isolated. These results can only be explained by cis-addition of nitrogen and Pd to the terminal double bond. The palladium-σ-complex trans-3a, formed from Z-1a, would give 2a by easy cis-elimination of "PdH". Stability of cis-3a would be ascribed to the absence of cis hydrogen to be eliminated.



Although cis-addition of nitrogen and Pd suggested initial coordination of amino group to Pd, no evidence was observed in the reaction of E- and Z-1a. However, on mixing Pd(II) with E- and Z-1b, having free amino group, immediate precipitaion of yellow powder was observed. This yellow powder was easily assigned as the expected Pd-complex 4b and proved to be the intermediate of amino-palladation reaction.



Further studies on the origins of preferential endo-closure to form azepines and cis-aminopalladation are now in progress and would be also presented.