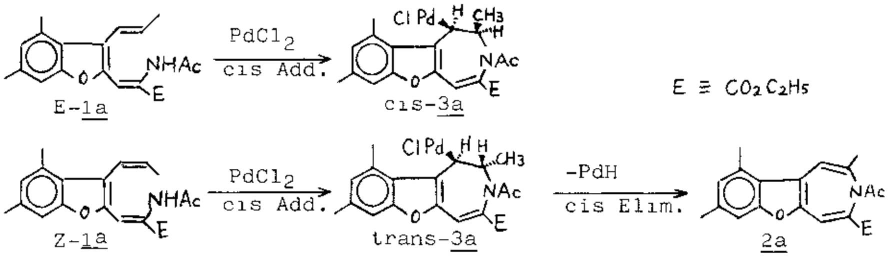
INTRAMOLECULAR AMINOPALLADATION REACTION OF 1-AMINOHEXATRIENE

Hiroshi Taniguchi, Hirotaka Yamasaki, Noriyuki Okada,
Kazuaki Isomura, and Shinjiro Kobayashi

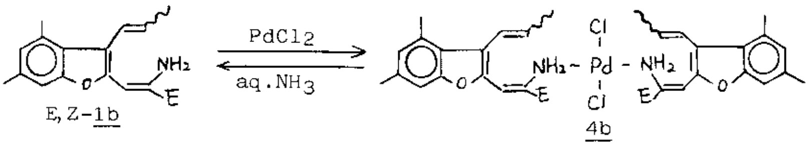
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka 812, Japan

We have recently found palladium promoted formation of azepines from 1-aminohexatrienes. 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$_2$CO$_3$, 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 aminopalladation 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.