The Interaction of Conjugated and Cumulative Dienes with Allylic Palladium Systems. The Nature of the Rate-determining Step for "Insertion" Reactions

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Summary The rate-determining step for "insertion" of 1,2- and 1,3-dienes into the allyl palladium bond is shown to be the actual insertion process, and not the initial co-ordination of the diene.

DIFFERENT mechanisms have been suggested for insertion of 1,2- and 1,3-dienes[1,2] into the allyl palladium bond, based upon the stereochemical nature of the products (III) and (IV). Kinetic data have been interpreted by assuming that the initial co-ordination of the diene to palladium is the rate-determining step.[2] We now report n.m.r. data which show that other mechanisms are operative, and that the rate-determining step in both cases cannot be either the co-ordination of the diene or the formation of the σ-allylic species (II).

Addition of allene or butadiene to 0.8M-CHCl_3 solutions of several π-allylic complexes of the type $(\pi\text{-all})\text{Pd}(X)$, (X = Cl, acetylacetonate, or hexafluoroacetylacetonate; ratio of diene:Pd $\leqslant 1$), at 37°, results in immediate collapse of the n.m.r. signals of the allylic syn- and anti-protons. This can only be caused by a rapid $\pi \rightarrow \sigma \rightarrow \pi$ process[3] involving reversible co-ordination of the diene to give a σ-allylic species (II). New signals due to insertion products (III) or (IV) are not observed until a later stage. The rate of the $\pi \rightarrow \sigma \rightarrow \pi$ process varies in the order L = allene > butadiene > 2,3-dimethylbutadiene; X = hexafluoroacetylacetonate > acetylacetonate $\simeq$ Cl; π-all = allyl > 2-methylallyl $\gg$ 2-t-butylallyl. Thus, the rate-determining step for product formation cannot be co-ordination of the diene, nor formation of a σ-allyl.

In contrast to the rate of $\pi \to \sigma \to \pi$ promotion, the rates of product formation from butadiene are much higher than those from allene, suggesting that two different mechanisms are operative and that the insertion of allene into a Pd–carbon σ-bond is much slower than the cyclic rearrangement for conjugated dienes.

X = Cl, acetylacetonate
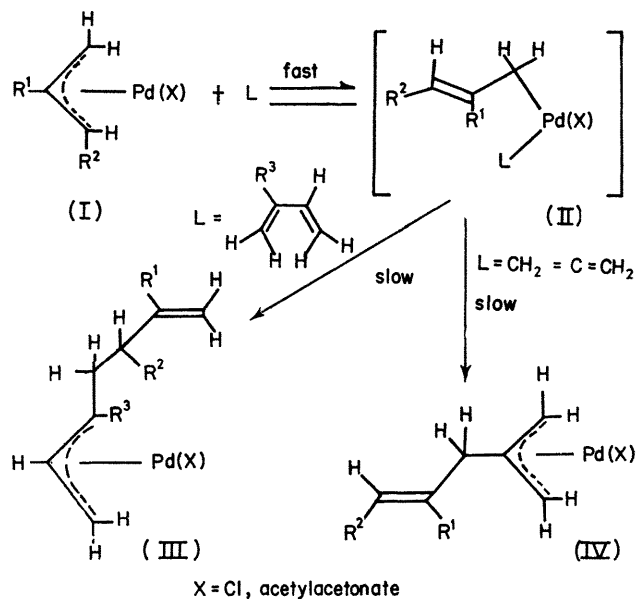
In systems where product formation readily occurs, the rate can be correlated with the relative stability of the σ-allylic intermediate (II) compared to its π-allylic precursor (I). Thus for a series of allyls (X = hexafluoroacetylacetonate; L = butadiene) the rate of product formation decreases in the order; allyl > 2-methylallyl $\gg$ 2-t-butylallyl. The free energy of activation of *syn–anti* proton exchange in the complexes [(π-all)Pd(OAc)PMe$_2$Ph] *via* a σ-allyl intermediate increases in the order allyl < 2-methylallyl < 2-t-butylallyl.[4]

Thus the rate-determining step in these reactions is the actual "insertion" process the rate of which is dependent on the mean lifetime of the σ-allylic intermediate (II), and is also, in the case of heavily substituted allyls and/or dienes, influenced by the thermodynamic stability of the product; *e.g.* when L = 1,3-di-t-butylallene; X = Cl or acetylacetonate; π-all = allyl; promotion of a $\pi \to \sigma \to \pi$ process is observed at 37°, but no insertion product is formed.

Although the rate of $\pi \to \sigma \to \pi$ promotion by allene was highest in π-allylpalladium hexafluoroacetylacetonate, no insertion of allene into the allyl palladium bond was observed. However, allene was consumed to yield oligomerisation products. Consequently, formation of oligomers cannot involve successive insertions into allylic palladium bonds.

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[2] D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 1969, **3**, 255.
[3] P. W. N. M. van Leeuwen and A. P. Praat, *Chem. Comm.*, 1970, 365 and references cited therein.
[4] J. Powell, submitted for publication in *J. Chem. Soc.* (*A*).