Tetrahedron Letters No. 15, pp 1363 - 1366, 1974. Pergamon Press. Printed in Great Britain.

THE STERIC COURSE OF THE PALLADIUM PROMOTED AMINATION OF SIMPLE OLEFINS[1]

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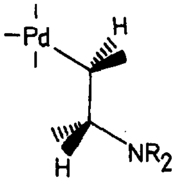
(Received in UK 12 February 1974; accepted for publication 4 March 1974)

A wide variety of nucleophiles have been observed to add to olefins complexed to palladium.[2]

When the nucleophile, *e.g.* acetate, is added externally *trans*-addition appears to take place.[2,3,4,5] With aryl- and alkylpalladium compounds, where the aryl and alkyl groups are essentially covalently bound to palladium, *cis*-addition occurs.[5] Chloride ion, which is more strongly co-ordinated to palladium than acetate, appears to add partially *cis*[5] and the same may be true for hydroxyl.[5]

We have recently shown that amines add to double bonds in high yields in an efficient palladium-promoted reaction. In this reaction the olefins show a reactivity pattern similar to that observed for olefins in cycloaddition reactions, *e.g.* *trans*-olefins are more reactive than the corresponding *cis*-olefins and cyclopentene is considerably more reactive than cyclohexene.[6,7] Since amines are strongly co-ordinated to palladium the amination could very well be *cis*. However, *trans*-addition has been observed for the corresponding platinum-promoted amination.[8] The amination with palladium is thus open to question and knowledge of the steric course of the amino-palladation is highly desirable. In this communication we report results from the palladium-promoted amination of 2-butenes, which show that the reaction proceeds *trans*.

The amination of *trans*- and *cis*-2-butene, respectively, produces two different σ-complexes 1 and 2.



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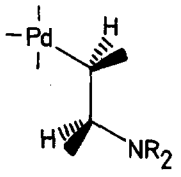

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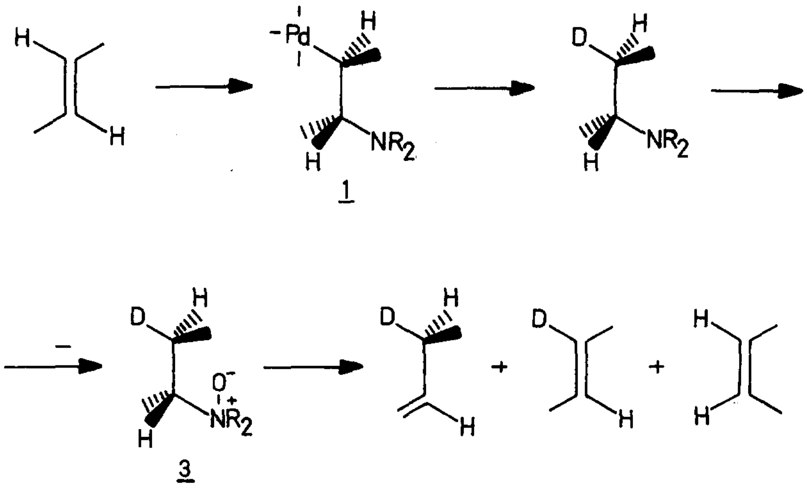
We first tried to establish the configuration of these complexes by NMR methods but sufficiently good NMR spectra could not be obtained due to the instability of the complexes 1 and 2. The following procedure was therefore used (Scheme 1): The complexes 1 and 2 were reduced at low temperature (-70°) with LiAlD$_4$.[9] The deuteriated amines obtained in this way were then converted to the *N*-oxides, for instance the compound 3, which after Cope elimination of hydroxylamine furnished a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene.[11] These olefins were separated by GLC and analysed for deuterium content by mass spectrometry (Table 1).



Within the experimental error (± 1 %) *cis*-2-butene was transformed into d$_1$-*cis*-2-butene with complete retention of the deuterium label as would be expected for stereospecific *trans*-amination followed by hydride reduction with retention of configuration[10] and stereospecific *cis*-Cope elimination.[12,13] The 1-butene that is formed simultaneously also retains the deteurium label (99± 1 %). However, the *trans*-2-butene, where deuterium would be expected to be eliminated also contains some deuterium (6 %). The amination-elimination sequence applied to *trans*-2-butene gave *trans*-2-butene and 1-butene retaining 95 % of the label and *cis*-2-butene containing 9 % of deuterium. These results are probably due to partial lack of stereospecificity in the reduction step, olefin isomerization and to the deuterium isotope effect in the Cope elimination (Table 1, refs. 14,15). For instance, if the amination-reduction sequence of *cis*-2-butene is 98 % stereospecific, the *cis*-2-butene formed in the elimination step would contain 99 % of deuterium and the *trans*-2-butene formed simultaneously would contain 6 % of deuterium in good agreement with the experimental results (Table 1). Compensating for a primary isotope effect of about 2.8,[13] the preference for the formation of *trans*-2-butene over *cis*-2-butene in the aminoxide elimination is 1.7 independent of the starting material (*cis*- or *trans*-2-butene).

TABLE 1

Butenes formed in the elimination step	From amination of *trans*-2-butene			From amination of *cis*-2-butene			Yield from undeuteriated aminoxide[11] (Cope *et al.*)
	relat. yield	% butene -h	% butene $-d_1$	relat. yield	% butene -h	% butene $-d_1$	
1-Butene	73.6	5	95	83.0	1	99	67.3
trans-2-Butene	21.8	5	95	6.5	94	6	21.0
cis-2-Butene	4.6	91	9	10.5	1	99	11.7

In conclusion, these results do not only show that the palladium-promoted amination proceeds *trans* but also prove the high stereospecificity (> 98 %) of the Cope elimination and of the hydride cleavage of palladium-carbon bonds.

Financial support from *KemaNord AB* and *The Swedish Board for Technical Development* is gratefully acknowledged.

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13. In the olefin-forming Cope elimination, an isotope effect is observed, K_H/K_D being approximately 2.6 for *cis*-2-butene and 2.9 for *trans*-2-butene. These figures agree well with the value 3.5 observed for the oxide of cyclooctyldimethylamine.[12c]

14. The olefin complexes were prepared *in situ* by stirring bis-benzonitrilepalladium dichloride in THF with a tenfold excess of the appropriate olefin for 30 min. at 0°. The mixture was then cooled to -40° and an excess of dimethylamine was added. After further cooling to -70°, $LiAlD_4$ was introduced. The deuteriated 2-butyldimethylamines obtained in this way contained none of the isomeric 1-butylamines. During the preparation of the olefin complex at 0°, about 2 % isomerization of *trans*-2-butene to the *cis*-compound was observed. At -50° and below, the isomerization was negligible. Similar results have recently been obtained with other olefins.[15]

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